THERMODYNAMICS AND STRUCTURE OF FLUIDS

PHYSISORBED ON NANOTUBES

A Thesis in
Physics
by
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Abstract

The thermodynamics and structure of atoms and molecules physically adsorbed (physisorbed) onto cylindrical surfaces at low temperatures is studied theoretically for two systems: classical argon adsorbed onto the external surface of a bundle of carbon nanotubes, and quantum molecular hydrogen adsorbed within a magnesium oxide nanopore.

The transition from quasi-one dimensional physics to two and three dimensional physics in these systems is characterized through analysis of density distributions, pair correlation functions, effective potentials, and heat capacities. The primary tool of investigation is Markov Chain Monte Carlo simulation of classical and quantum statistical mechanics. Semi-analytic results are also obtained for one dimensional, quasi-one dimensional, and two dimensional systems.
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Chapter 1

Introduction

1.1 Surface adsorption

1.1.1 Types of adsorption

Surface adsorption is the process by which atoms and molecules (generically: “particles”, “adsorbates”, “adatoms”) adhere to surfaces (generically: “substrates”) by their mutual attraction. This attraction may be due to chemical bonding (chemical adsorption, or “chemisorption”), or by long-range van der Waals forces (physical adsorption, or “physisorption”).

This dissertation is concerned solely with the latter process, of physical adsorption. Physisorption is simpler to study theoretically because the gas-gas interactions are well known from gas phase studies, and are not altered by the presence of the surface. Physisorption is also of interest at low temperatures—and therefore in the study of quantum gases—because it is weaker than chemisorption. With large adsorbate-substrate binding energies, chemisorbed particles are essentially “welded in place” onto the substrate at low temperatures when little thermal energy exists in the environment. The smaller binding energies of physisorption mean that at low temperatures the particles are free to both adsorb onto and “desorb” (i.e., become unbound) from the substrate; they can move around freely on the surface as a fluid; their thermodynamic behavior is more sensitive to variations in temperature and pressure.

Thus, at low temperatures, the weak physisorption of particles that do not chemically react with their substrates is the more interesting phenomenon to study. Theoretical and experimental results in physisorption are reviewed in Bruch, Cole, and Zaremba [1]. The energy threshold below which physisorption occurs may be somewhat arbitrarily taken to roughly equal 0.3 electron-volts (corresponding to a temperature of 3500 K), although any such boundary between physical and chemical adsorption is subjective.
The adsorbates most studied in physisorption are nonpolar (so that permanent dipole moments can be neglected) and spherical (which can be modeled by a simple radial potential). Often they are noble gas atoms, because they do not bond chemically to other atoms. Indeed, were it not for van der Waals attraction, the inert gases would be essentially noninteracting and could not exist in condensed phases.

The van der Waals forces—or more specifically, the London dispersion forces—responsible for physisorption occur when the spontaneous quantum fluctuation of a molecule’s electric dipole moment induces a dipole moment in a neighboring molecule, giving rise to a long-range mutual attraction. At short range, the charges in neighboring molecules begin to overlap, giving rise to a repulsion. At some intermediate range, given by the minimum of the intermolecular potential, there is a stable equilibrium separation at which the molecules will prefer to remain.

The intermolecular potential is often taken to have the semiempirical Lennard-Jones “12-6” form, which depends only on the intermolecular separation $r$ between two molecules,

$$V(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6\right], \quad (1.1)$$

where $\epsilon$ and $\sigma$ are parameters characterizing the potential well depth and equilibrium separation, respectively. The $r^{-6}$ nature of the long-range attractive term in the potential is characteristic of London dispersion forces due to induced dipoles, and can be derived within the context of second-order perturbation theory. The total system energy is taken to be a pairwise sum of these 2-body potentials, neglecting 3- and higher-body interactions. Intermolecular potentials for surface adsorption are reviewed in Vidali et al. extended derivations of the surface plasmon theory describing adsorbate-substrate physisorption potentials are found in Schmeits and Lucas.

1.1.2 Applications

Surface adsorption finds industrial application in areas such as filtration, in which unwanted particles are trapped on the surface of a filter, and in storage, the conceptually opposite yet physically identical process in which desired particles are kept bound to a surface. Adsorption can be used to coat surfaces with other substances in order to alter their chemical, mechanical, or dielectric properties. In surface chemistry, a substrate can catalyze the adsorbate via chemisorption. Surfactants find some everyday application, such as when detergent helps water to

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At large distances the strength of the dispersion interaction changes to a Casimir-Polder $r^{-7}$ behavior due to “screening” from retarded interactions, arising from the finite propagation speed of light, but this happens at distances great enough to be largely irrelevant in the denser condensed phases of matter; for one exception, see [4].
wet fabric and suspend removed particles in solution, or when they help paint to apply smoothly and adhere to surfaces.

1.1.3 Restricted geometries

From the perspective of a theoretical physicist, one of the most interesting aspects of surface adsorption is the study of restricted geometries, wherein particles are not free to move in every direction. Even though our world is three dimensional (3D), particles bound to a surface may behave as if space were two dimensional (2D); confined inside a very thin tube such as a nanotube, the particles may even behave as if they existed in a one dimensional (1D) space.

Physics can be very different in low dimensions (\(D < 3\)). Thermodynamically, the Mermin-Wagner-Hohenberg theorem \([7, 8, 9, 10, 11]\) establishes the absence of broken continuous symmetries and long-range order at finite temperature\(^2\) \((T > 0)\) in \(D < 3\), implying that second-order phase transitions of the standard symmetry-breaking type do not exist in low dimensions.\(^3\) The earlier theorem by van Hove places limitations on the existence of phase transitions in 1D in systems with short-range interactions \([13, 14]\). Other phase transitions outside the Landau symmetry-breaking paradigm are possible, however; in 2D, the Berezinskii-Kosterlitz-Thouless topological phase transition \([15, 16]\) is a famous example, with relevance to the XY ferromagnetic spin model, superfluidity, and superconductivity. In a closely related result, Hohenberg’s theorem \([8]\) also implies that Bose-Einstein condensates (BECs) cannot form in low dimensions, even in 2D films of finite thickness \([17]\).\(^4\) Exotic topological spin statistics (“anyons”), other than the usual Bose-Einstein and Fermi-Dirac statistics, can exist in \(D = 2\) \([19]\).

Restricted geometries can also alter the character of interacting systems simply by decreasing the number of particles that neighbor other particles. For instance, the freezing point of a solid will generally be reduced in low dimensions: there are fewer nearby atoms in a crystal lattice to bind a particular atom in place, allowing thermal energy to keep the system fluid at temperatures for which the bulk 3D system would solidify from its stronger interparticle binding.

The interest in adsorption in restricted geometries, then, encompasses questions such as: What does theory predict will happen—e.g., concerning the thermodynamic behavior or structural characteristics of the adsorbate—in a restricted geometry? Do experiments agree? What kinds of substrates and surface geometries—weakly or strongly binding, flat or curved, homogeneous or inhomogeneous, ordered or disordered—give rise to novel effects, or enhance known effects to the greatest

\(^2\)There exist generalizations of this result to zero temperature \([12]\).
\(^3\)The fine print on the theorem must be read, and it is not as generally applicable as is sometimes supposed. For instance, two dimensional crystals can exist with broken rotational symmetries, although not broken translational symmetries \([10]\).
\(^4\)There is fine print here too. BECs can form in inhomogeneous systems for \(D < 3\), such as in trapped gases; see, for instance, Ref. \([18]\) and references therein.
degree? When do restricted geometries give rise to physics in low dimensions, and to what extent? Under what conditions does the adsorbate behave one dimensionally? Two dimensionally? Three? Four? (1)\(^5\) Does anything unusual (thermodynamically or structurally speaking) occur as a system transitions from one dimensionality to another? Such questions are the focus of this dissertation.

1.2 Carbon nanotubes

1.2.1 Nanotube properties

Carbon nanotubes (henceforth: nanotubes) are tubular fullerene molecules composed entirely of carbon atoms (Fig. 1.1). Structurally, they consist of one or more graphite-like sheets wrapped to form concentric cylindrical shells. Nanotubes with single or multiple shells, or “walls”, are referred to as single-walled nanotubes (SWNTs) or multiple-walled nanotubes (MWNTs), respectively. The trivalent carbon atoms in an individual shell are bonded to each other in a hexagonal graphitic network, with pentagonal/heptagonal defects to introduce local curvature (Fig. 1.2). A typical carbon nanotube is some 1–2 nm in diameter and can be microns in length.

![Figure 1.1. Carbon nanotubes.](http://www.sdm.buffalo.edu/scic/gallery.html)

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\(^5\)Concerning the possibility of Bose-Einstein condensation in four effective dimensions, see [20].
Nanotubes are found in both open and closed (capped) forms. Nanotubes that are closed, which is the most common natural state of a nanotube, can be thought of as elongated buckminsterfullerenes ("buckyballs"). Closed nanotubes can undergo treatment to open the ends via chemical means (a nitric acid bath, or oxygen at high temperatures) or by the application of large electric fields. Open nanotubes allow for adsorption into the interior of the nanotube (although adsorption within a closed nanotube can occur if the nanotube forms around the adsorbate when it is created; see Fig. 1.3). This is possibly the most intriguing application of nanotubes, from the perspective of surface adsorption. For a survey of adsorption on carbon of various forms, including carbon nanotubes, see [21].

Nanotubes have many interesting physical properties. Most important to the field of adsorption in restricted geometries, they are very nearly one-dimensional objects: their length/diameter aspect ratio can be as great as $10^4$. Structurally, they are extremely strong: their tensile strength can exceed 150 GPa and their Young’s modulus is on the order of 1 TPa [23, 24, 25, 26]. Electrically, they can be either metallic or semiconducting, depending on their chirality (winding), capable of sustaining high current densities in excess of 1 A/cm² at 60 V [27]. Their thermal conductance is high, above 3000 W/mK near room temperature [28, 29].

The history and properties of carbon nanotubes are reviewed by Dresselhaus, Dresselhaus, and Avouris [30]; Dresselhaus, Dresselhaus, and Eklund [31]; Ebbe-
Figure 1.3. A “bucky peapod”: spherical $C_{60}$ buckminsterfullerene molecules adsorbed within an open, single-walled carbon nanotube. [Source: Smith, Monthioux, and Luzzi [22].]

ten [32], Yakobson & Smalley [33], and Schönenberger & Forró [34], among many others.

1.2.2 Nanotube applications

The technological applications of nanotubes are numerous [35, 36]. Nanotubes can be wetted, drawing fluids within them by capillary forces [37]. The uptake of material within nanotubes can be used as filters for chemical and biological separation of matter of different sizes and interactions [38]. They can be used as mass conveyors or conduits [39]. Mechanically, nanotubes can be used as motors or in micro-electro-mechanical systems (MEMS) [40]. Their electrical properties lead to their use in nanowires and nano-circuits [41, 42, 43], field effect transistors [44, 45], field emission displays [46], and “ultracapacitor” batteries [47], among other applications. Structurally, they are strong, light alternatives in the family of carbon fiber composites [23, 48]. The van der Waals interactions of nanotubes make them suitable for use in adhesives, similar to the structure of gecko foot hairs [49]. They can be used as scanning microscope probes [50].

1.2.3 Nanotube bundles

The production of carbon nanotubes in the laboratory by processes such as arc discharge, laser ablation, and chemical vapor deposition typically results not in a collection of individual nanotubes, but in bundles consisting of a number of nanotubes adhering to each other [32] (Fig. 1.4). Such bundles provide three sites for the adsorption of external molecules: the interiors of the nanotubes, the interstices within the bundle between neighboring nanotubes, and the exterior
surface of the bundle (Figs. 1.5, 1.6). All three are interesting and have been considered in the literature; this dissertation is concerned with the latter case (Chapter 2). It is similar to planar surface adsorption, but with a more interesting corrugated geometry (Fig. 1.7).

**Figure 1.4.** A tangle of carbon nano-fibers (above), 10–20 nm in thickness, which are bundles consisting of carbon nanotubes arranged in a triangular lattice (below). [Source: B. I. Yakobson and R. E. Smalley [33].]

### 1.3 Porous materials

Carbon nanotubes are not the only means by which particles can be confined in quasi-one dimensional geometries. There exists a variety of porous media, in which small pores permeate a bulk solid or membrane. For instance, “nucleopores” are formed by chemically etching the linear tracks left by heavy ion bombardment of a material, and can have diameters as small as 50 nm. Even smaller pores can be synthesized by various means, such as nanotemplating, in which microscopic structures (colloids, latex spheres, etc.) are used as templates around which pores
can be formed; such processes can lead to materials containing pores as small as a few nanometers, only slightly wider than carbon nanotubes [51, 52]. Figure 1.8 depicts a nanopore in bulk MgO.

The applications of nanopores are similar to those of carbon nanotubes (minus the novel structural strength and electrical properties of nanotubes): filtration, storage, and catalysis. Nanoporous membranes, in particular, are often used to sieve and separate. Indeed, from the perspective of adsorption geometry, there is often little difference between nanotubes and nanopores, other than the fact that nanopores are larger (and can be much larger): they are both 2D cylindrical geometries (or quasi-one dimensional, depending on the size of the tube/pore relative to the adsorbate). Nanotubes, of course, allow for adsorption on the outside of the
Figure 1.7. End-on (cross sectional) view of a groove region on the exterior surface of a nanotube bundle. The view is along the bundle’s longitudinal ($y$) axis; the vertical ($z$) axis is normal to the bundle surface. Depicted are portions of two neighboring nanotubes (shaded quarter circles), and the Ar-nanotube isopotential surfaces (in kelvins). The groove is the potential minimum at $-1600$ K.

tubes (or between tubes in bundles) as well as inside the tubes, while nanopores only allow for adsorption within the pores. Nanotubes can also be fashioned to project off of surfaces, and can tangle in complex fashion, while nanopores are linear cavities within surfaces.

1.4 Overview

This dissertation is organized around two major projects. The first project (Chapter 2) studies argon atoms, treated as classical point particles, adsorbed onto the exterior surface of a bundle of carbon nanotubes. As the density, or coverage, of the adsorbed Ar increases, the system transitions from a quasi-one dimensional phase to a two-dimensional film. The heat capacity of the adsorbate, measuring the change of energy in the system as its temperature is increased, peaks at two temperatures: the lower temperature corresponds to thermal excitation of particles about their existing adsorption sites, and the higher to thermal excitation of particles into new sites elsewhere on the bundle surface. The thermodynamics of this system are compared to experimental results and agree at high coverages, but disagree at low coverages due to our idealized assumption of a bundle consisting
of nanotubes of identical size.

The second project (Chapter 3) studies hydrogen molecules, treated quantum mechanically, adsorbed within the interior of a magnesium oxide nanopore. Small pores confine the hydrogen one-dimensionally on the pore axis, while larger pores allow the hydrogen to plate the inner surface of the pore in a two dimensional film. The critical pore size at which the transition between these structures is determined by several complementary numerical methods. Dimer structure, with hydrogen molecules binding weakly to each other, is seen in the system at low temperatures. The heat capacity of the hydrogen calculated in the noninteracting limit shows a clear transition from the thermodynamics of a 1D system to those of a 2D system as the pore size is increased past the critical size, and a quasi-one dimensional approximation to the system’s thermodynamics is shown to be valid for small pores in which the adsorbate is nearly one dimensional.

The primary tool of investigation in this work is Monte Carlo simulation (App. B),\textsuperscript{6} which is well suited to calculating thermodynamic quantities which can be expressed as ensemble averages of probability distributions: the Markov Chain Monte Carlo method approximates population means by simulated sample means.

\textsuperscript{6}The main competitor to Monte Carlo simulation is molecular dynamics simulation [53], which was not utilized in this work.

\textbf{Figure 1.8.} A MgO nanopore, 100 nm in diameter. [Source: Jiu et al. [51].]
Since the theoretical framework of statistical mechanics is founded on probability distributions—particularly the Boltzmann distribution in the canonical ensemble which governs the probability of a particle existing in a particular energy state—the class of thermodynamic observables accessible to Monte Carlo simulation is large, and includes the heat capacity. In addition to Monte Carlo simulation, many numerical and analytic results were derived in Mathematica \cite{54}, and some statistical analysis was done with the R programming language \cite{55}.

Conventions

Except when noted otherwise, units are used in this thesis such that the Boltzmann constant $k_B$ equals unity, so that it does not appear in equations. The equation $E = k_B T$ implies that in these units, energies can be measured in kelvins; the conversion factor of $k_B$ means that $1 \text{ eV} = 11605 \text{ K}$. 
Chapter 2

Argon adsorbed on the exterior of a bundle of carbon nanotubes

2.1 Introduction

One motivation for studying nanotube bundles is that adsorption onto such a geometry provides the possibility of a transition in the adsorbate structure from a quasi-one dimensional to two-dimensional geometry. (At higher pressures, the coverage increases to form a fully three dimensional bulk solid adsorbed on the substrate.) The structure of these 1D and 2D phases is discussed in Sec. 2.2, and their thermodynamics in Sec. 2.3.

The substrate we examine is the region near two neighboring SWNTs, of diameter 13.8 Å, on the surface of the nanotube bundle (Fig. 2.1). The bundle is homogeneous by assumption: all nanotubes have identical sizes, forming a static and perfect lattice. We further assume the nanotubes are closed, so that no gas can adsorb inside them, and we further neglect the possibility of interstitial adsorption within the bundle.\(^1\) The nanotubes are treated as infinite, perfect cylinders (neglecting the graphitic structure of the underlying carbon atoms), and their adsorption potential is of the Lennard-Jones form integrated over the cylindrical surface \(^57\).

We chose to study argon as the adsorbate. It is a weakly interacting noble gas, ideal for studying physisorption. It is spherical and nonpolar, making it easily modeled by a spherically symmetric Lennard-Jones 12-6 potential. It is massive enough to act classically at temperatures and densities of interest,\(^2\) allowing us

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\(^1\)The assumption of no interstitial adsorption is plausible for argon adsorbed on homogeneous bundles of SWNTs \(^56, 57, 58\). The status of interstitial adsorption for other adsorbates, such as He and H\(_2\), is more controversial \(^59\).

\(^2\)The classicality of a system is dictated by the thermal wavelength of its particles compared to the density of the system. A discussion of the thermal wavelength may be found in Appendix A.1.
Figure 2.1. End-on (cross sectional) view of a groove region on the exterior surface of a nanotube bundle. The view is along the bundle’s longitudinal ($y$) axis; the vertical ($z$) axis is normal to the bundle surface. Depicted are portions of two neighboring nanotubes (shaded quarter circles), and the Ar-nanotube isopotential surfaces (in kelvins). The groove is the potential minimum at $-1600 \text{ K}$. See Figs. 1.5 and 1.6 for an overview of the nanotube bundle surface geometry.

to ignore the complexities of the Monte Carlo simulation of quantum mechanical systems (see Secs. 2.5.5 and 2.5.6.1 for further discussion of this point). We treat it as a classical point particle, neglecting all internal degrees of freedom.

In Section 2.2, we study the structure of the adsorbed argon, in its “groove”, “three-stripe”, and “monolayer” adsorption phases. Most of the work, however, focuses on the thermodynamics of the argon film (Sec. 2.3), particularly its heat capacity (Sec. 2.3.1). At higher adsorption coverages, a characteristic double-peaked structure appears in the temperature dependence of the heat capacity (Sec. 2.3.3), with a low temperature peak arising from dispersion of Ar within the groove between neighboring nanotubes (“energy broadening” or “thermal broadening”), and a higher temperature peak arising from excitation of Ar from the groove site into the monolayer (“promotion”). These results were facilitated by use of the Wang-Landau Monte Carlo algorithm, one of a family of newer “broad histogram” Monte Carlo methods (Sec. 2.3.2). The simulated thermodynamics were compared to experimental measurements as well as other simulation predictions (Sec. 2.3.4), and were found to be in agreement with experiments except at low coverages, due to our simulations’ unrealistic assumption of uniform nanotube sizes in the bundle.
2.2 Adsorbate structure

Consider again the nanotube bundle geometry in Figure 2.1. At low densities, the adatoms will primarily adsorb at the location of the minimum argon-nanotube ("external") potential, along the 1D line forming the groove between two neighboring nanotubes. As the density increases, adatom-adatom repulsion will prevent all of the adatoms from adsorbing in the groove; the groove will fill and the remaining atoms will begin to cover the remainder of the bundle surface with a monolayer. At intermediate densities, a so-called “three stripe” (3-stripe) phase forms, a partial monolayer in which the adsorbate occupies the linear groove as well as two parallel lines higher up on the nanotube surfaces. At higher densities, a full monolayer forms consisting of a number of parallel stripes completely plating the surface in 2D; at still higher densities, bilayers and other structures form. These phases of adsorption, produced by Metropolis Monte Carlo simulation in the canonical ensemble, are depicted in Figure 2.2.\(^3\)

The Ar structure may be further examined through use of the pair correlation function, which gives the probability of two Ar atoms having a given relative displacement (Fig. 2.9). For the purpose of comparison to experiment, the correlation function is a more useful encoding of the film structure than is the adsorbate density distribution, because it may be related to surface diffraction measurements via Fourier transformation. This is the first such structure prediction for Ar adsorbed on a nanotube bundle. Results for the pair correlation function are discussed in more detail in Sec. 2.5.3, including evidence of the argon film melting near \(T = 90\) K.

2.3 Adsorbate thermodynamics

The primary result achieved this work was the discovery of a double-peaked structure in the temperature dependence of the adsorbate heat capacity, by means of the Wang-Landau algorithm, a modern Monte Carlo simulation method first applied to a problem of surface adsorption by this work.

Below we discuss the thermodynamic concept of heat capacity, its calculation via Monte Carlo simulation, our heat capacity results for the argon+bundle system, and comparison of these results with other theoretical as well as experimental work.

\(^3\)Although the simulated system (two parallel infinite cylinders) is translationally invariant in the longitudinal (axial) direction, the simulations in the bottom plots of Fig. 2.2 spontaneously break translational invariance over finite simulation time: instead of adsorbing with equal likelihood uniformly along lines, they adsorb at particular positions along those lines, without sufficient Monte Carlo time for them to diffuse everywhere in the simulation cell (the problem of correlated samples).
Figure 2.2. Left, middle, and right: the groove, 3-stripe, and monolayer phases of adsorption. The dots depict probable locations of Ar atoms (the adsorbate density distribution). Above: end-on (cross sectional) view of the nanotubes (compare Fig. 2.1). Below: overhead view of the nanotubes (nanotube axis runs vertically through the center of each figure). These figures were produced from a number of superimposed Monte Carlo configurational samples generated at \( T = 45 \) K. The regular crystalline structure indicates a solid phase at this temperature.

2.3.1 Heat capacity

The (isochoric) heat capacity \( C_V(T) = (\partial E/\partial T)_{N,V} \) is the rate of change of energy with temperature at constant system volume and particle number.

The heat capacity is peaked (attains local maxima) when a given change in temperature results in a relatively large change in energy. This can occur, for instance, when adatoms migrate to new locations with significantly different values of the external (adsorbate-substrate) potential energy; this is called “promotion” or sometimes ”excitation”. It can also occur when adatoms remain in roughly the same location on average, but spread out over a greater volume and therefore
greater range of potential energies; this is referred to as “energy broadening” or “thermal broadening”.

It is easy to see why promotion leads to a larger heat capacity: it occurs when the temperature increases to the point that the available thermal energy allows significant numbers of adatoms to be excited into regions of higher potential energy, leading to an increase in total system energy.

It may not be as clear, however, why energy broadening can also lead to an increase in heat capacity. Although the particles remain in more or less the same average position, their average energy can increase: for instance, if they spread out over a larger region of space near a potential minimum, their average position may remain at the potential minimum, but their average energy will increase when more particles move away from the minimum.

The relationship between energy broadening and heat capacity may be elucidated by noting that in the canonical ensemble, the heat capacity is also proportional to the mean-square fluctuation in energy, $C_V(T) = \langle (\delta E/T)^2 \rangle$ (App. A.2.1). Thus, increasing fluctuations in energy away from the average energy lead to increasing heat capacities.

The fluctuation form of the heat capacity is was used to calculate the heat capacities in our simulations: it can be written purely in terms of ensemble averages, $C_V(T) = \langle E^2 \rangle - \langle E \rangle^2 / T^2$, and so is amenable to Monte Carlo calculation. The alternative, as far as numerical methods are concerned, is to write it in its original differential form $C_V(T) = (\partial E/\partial T)_V$ and approximate the derivative numerically as a finite difference $C_V(T) \approx [E(T + \delta T) - E(T - \delta T)]/(2\delta T)$. However, because this requires two Monte Carlo simulations for each temperature $T$ at which the heat capacity is to be calculated, and ensemble averages have to be calculated anyway (for the average energy $E \equiv \langle E \rangle$ at $T \pm \delta T$), it is no more difficult to calculate the average $\langle E^2 \rangle$ and use the fluctuation formula to determine the heat capacity with a single simulation at temperature $T$. This may also introduce less error than two averages calculated at different temperatures with the addition of two-point finite difference error.

### 2.3.2 Wang-Landau Monte Carlo calculation of heat capacity

Starting from the fluctuation formula for heat capacity,

$$C_V(T) = \frac{\langle E^2 \rangle - \langle E \rangle^2}{T^2}, \quad (2.1)$$

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4 The energy fluctuation is defined as $\delta E \equiv E - \langle E \rangle$.

5 From the preceding fluctuation formula it can be shown that the heat capacity will increase with temperature as long as the mean-square energy fluctuation $\langle (\delta E)^2 \rangle$ increases faster than linearly with temperature.
the traditional Metropolis Monte Carlo algorithm will proceed by approximating the expectation values $\langle U \rangle$ and $\langle U^2 \rangle$ for a system at fixed temperature $T$ as sample averages, with sample configurations $x$ drawn from the Boltzmann distribution, $p(x) \sim \exp\left[-\beta U(x)\right]$.

The Wang-Landau algorithm departs substantially from this method of calculating ensemble averages. It calculates sample means, but only indirectly. It exploits the concept of the "density of states", $g(E)$, defined such that $dx = g(E)\, dE$, where $x$ is a state vector. The density of states is a probability density function which can be interpreted as the volume of phase space—or "number of states"—corresponding to an infinitesimal range of energy: the probability $g(E)$ of randomly chosen microstate being found in a small interval about the total system energy $E$.

The density of states can be used to express an expectation value as an average over energies $E$ instead of microstates $x$. For instance, in the canonical ensemble the average energy may be written,

$$\langle E \rangle = \frac{1}{Z} \int_{\text{states}} dx \, E(x) \exp\left[-\beta E(x)\right] = \frac{1}{Z} \int_{\text{energies}} dE \, E \, g(E) \exp\left(-\beta E\right), \quad (2.2)$$

where $Z$ is the partition function.

We can then approximate the expectation as an average over $n$ samples drawn uniformly from phase space, or as a weighted average of samples—weighted by the density of states—drawn uniformly from "energy space",

$$\langle E \rangle \approx \frac{1}{Z} \sum_{i} E(x_i) \exp\left[-\beta E(x_i)\right] \approx \frac{1}{Z} \sum_{i} E_i \, g(E_i) \exp\left(-\beta E_i\right), \quad Z \approx \sum_{E_i} g(E_i) \exp\left(-\beta E_i\right). \quad (2.3)$$

At this point, one might be tempted to dismiss these manipulations as mere formalism. What has writing expectations in terms of the density of states gained us over the traditional Metropolis algorithm? The main advantage for the purposes of the present work comes from the simple observation that the density of states $g(E)$—or rather, in practice, $g(U)$—is a function of energy only: it is independent of temperature. Thus by performing a Monte Carlo simulation that

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6As usual, we integrate out momentum/kinetic degrees of freedom exactly in closed form by the classical equipartition theorem $\langle K \rangle = \frac{3}{2}k_B T$ (in 3D), so that $\langle E \rangle = \frac{1}{2}k_B T + \langle U \rangle$, and we have to calculate only the position/potential/configurational degrees of freedom.

7Here, $E$ refers to the total system energy, not to the energy of an individual particle.

8Strictly speaking, the density of states is a quantum concept arising from the energy spectrum given by the Schrödinger equation. However, it may be applied to classical statistical mechanics by means of the semiclassical phase space quantization, wherein the volume of classical phase space $d\omega$ corresponds to $d\omega/(N!h^{3N})$ distinct quantum states.

9From the expression $Z(\beta) = \int dE \, g(E) \exp\left(-\beta E\right)$, we recognize the partition function as the Laplace transform of the density of states.
averages over energy samples instead of configurational samples, we can calculate \( \langle U \rangle \) or any other expectation at any \( \beta \) (or equivalently, \( T \)) from the output of a single “temperatureless” simulation.

The Wang-Landau algorithm operates by dynamically estimating \( g(U) \) while it is diffusing through energy space and generating energy samples.\(^{10}\) Once \( g(U) \) is determined, the expectation values \( \langle U \rangle \) and \( \langle U^2 \rangle \) can be calculated. Indeed, the partition function itself and all thermodynamic derivatives can be calculated—something impossible to calculate directly with Metropolis Monte Carlo, although this benefit was not exploited in the present work.

In Figure 2.3 the (configurational) density of states (“per particle”) \( g(U/N) \) is depicted for various phases of adsorption. Note that the ground state (below which the density of states is undefined) for the groove phase \((N = 9)\) is near \(-1720\) K, somewhat below the value of the Ar-bundle external potential minimum of \(-1600\) K; this is because the total energy \( U \) is the sum \( U_{\text{ext}} + U_{\text{int}} \) of the external potential and the Ar-Ar interaction energy; the latter is \(-120\) K at equilibrium separation. The 3-stripe and monolayer ground state energies are above \(-1600\) K because the adatoms are largely at higher external potential energies; the monolayer ground state energy is slightly higher than the 3-stripe energy, as expected.

Some further details regarding the application of the Wang-Landau algorithm may be found in Sec. 2.5.2.

### 2.3.3 Heat capacity for argon on a nanotube bundle

Figure 2.4 depicts the heat capacity results obtained for the argon+bundle system via Wang-Landau Monte Carlo simulation. Plotted is the specific heat, or heat capacity per particle \( C_V(T)/N \). For purposes of comparison, the Wang-Landau results are compared with those of the Metropolis algorithm in Figure 2.5.

We first turn our attention to the interesting double-peak structure in the heat capacity. All of the phases show a large peak in the heat capacity near \( T = 175\) K. This peak is interpreted as due to promotion of Ar atoms, specifically from the groove into the monolayer.\(^{11}\) The groove, 3-stripe, and monolayer phases show an additional peak at lower temperatures below 100 K. This peak is interpreted as due to energy broadening. The low density case lacks a corresponding lower temperature peak; the absence of this peak is attributed to the fact that a low density gas is essentially non-interacting, and therefore without interparticle repulsion there is less incentive for the adatoms to fluctuate from the potential minimum to produce

\(^{10}\)What is actually calculated is the relative density states, which is the density of states up to an unknown constant of proportionality.

\(^{11}\)The location of this peak implies an energy barrier of 875 K using the “2/5 rule” (App. A.2.2), which tallies well with the actual groove-monolayer energy gap of 820 K; see the value of \( |V_g - V_m| \) in Eq. 2.5.
Figure 2.3. Logarithm of the ("per particle", relative, configurational) density of states, $\ln g(U/N)$, for the low-density limit ($N = 1$) and the groove ($N = 9$), three-stripe ($N = 27$), and monolayer ($N = 54$) phases. The density of states is normalized to unity for each phase at its lowest energy. For an enlarged view of the density of states (not its logarithm) for the $N = 1$ case, see Figure 2.15.

energy broadening.

These interpretations are supported by a study of the external potential energy distributions of individual adatoms, detailed in Sec. 2.5.4, depicted in Figure 2.11, and summarized in Table 2.1. In order to distinguish between promotion and energy broadening, the particles were divided into energy regimes corresponding to the groove, monolayer, and vapor regions of the bundle. If particles moved from one energy regime to another as temperature increased, the heat capacity increase was attributed to promotion; if they stayed in the same regime but their distribution of energies spread out, becoming less concentrated at a minimum energy, the heat capacity increase was attributed to energy broadening.

The low density heat capacity was also compared to that of the “dimensional crossover” model (Sec. 2.5.4.2), an exactly solvable toy model in which the groove to monolayer promotion is transparent. In this model, the groove region is treated as a 2D, cylindrical harmonic potential, and the monolayer region is treated as a
1D, planar harmonic potential; all other regions are ignored, as are interparticle interactions. Because this model is completely quadratic (harmonic), its partition function can be solved exactly by Gaussian integrals.

The low density Monte Carlo results and the dimensional crossover model both have peaks in the heat capacity at $T \approx 175$ K. The peak in the crossover model can directly be shown to be due to groove to monolayer promotion. This supports the hypothesis that the similarly located peaks for the higher density phases are also due to groove to monolayer promotion. However, it says nothing about the lower temperature peak, which is absent in both the low density simulations and the dimensional crossover model. Furthermore, the low density heat capacity peak calculated by Monte Carlo is some 40% greater in magnitude than the dimensional crossover model’s peak. This suggests that the crossover model is only qualitatively reliable, as it neglects the true anharmonic character of the Ar-bundle external potential. For further discussion of these results, see Sec. 2.5.7.1.
Figure 2.5. A comparison of the specific heats calculated by the Wang-Landau and Metropolis methods. Solid curves are the all-temperature Wang-Landau simulations from Figure 2.4; symbols are from individual Metropolis runs at specific temperatures. Heat capacities are calculated by the fluctuation formula Eq. 2.3; Metropolis uses the first equation given there and Wang-Landau uses the second.

We now turn our attention to the high and low temperature limits of the heat capacity. A 3D noninteracting gas has a specific heat of $\frac{3}{2}$; from the equipartition theorem, a specific heat of $\frac{1}{2}$ is contributed from each of the three directions in which a particle may have momentum. The specific heats of all phases of Ar adsorption in Figure 2.4 approach this value at high temperatures, indicating full evaporation of the Ar film off the substrate into a 3D vapor.

A 3D solid has a specific heat of 3: in addition to the kinetic contribution of $\frac{3}{2}$, it receives (again, by the equipartition theorem) a potential contribution of $\frac{1}{2}$ from each direction in which a particle in the solid may be confined by interaction with its neighbors. The specific heats of the groove, 3-stripe, and monolayer phases all have this value at low temperatures, which requires some additional explanation.

A 1D solid has a specific heat of $\frac{1}{2} + \frac{1}{2} = 1$, and a 2D solid a specific heat of $1 + 1 = 2$. The monolayer phase is ostensibly a 2D solid, but the film is only quasi-two dimensional: in addition to the 2 degrees of freedom of motion and the 2
degrees of confinement due to neighboring Ar atoms in the solid film, the adatoms can move in a third direction perpendicular to the film; they are also confined in this direction, not by neighboring adatoms, but by the external nanotube potential attracting them to the bundle. This leads to additional contributions of $\frac{1}{2}$ from kinetic motion and potential confinement, bringing the specific heat up to that of a 3D solid in which the atoms are free to move in and are confined in all three dimensions.

The “1D” groove case is similar to the monolayer: the adatoms are free to move in all three dimensions, and are confined in all three dimensions, giving a specific heat of 3 as well. The only difference is that in the monolayer case, two dimensions of confinement were due to neighboring atoms: and one was due to confinement by the external potential; the opposite is true for the groove, in which one dimension of confinement is due to neighboring groove atoms, and two dimensions of confinement are due to external potential (note the circular contours of the external potential in Fig. 2.1).

The 3-stripe phase has an analogous low temperature specific heat of 3 like the other two phases, although the separation of confinement into “neighbor interaction” and “substrate interaction” degrees of freedom is not as clear. The low-density case, on the other hand, has a low temperature specific heat of $\frac{5}{2}$: it is like the groove phase, but the density is low enough that there are not enough neighboring adatoms in the groove to confine a given adatom in the longitudinal direction, subtracting $\frac{1}{2}$ from a potential degree of freedom.

2.3.4 Comparison with other work

The heat capacity of argon adsorbed on carbon nanotube bundles has been studied via Monte Carlo simulation by grand canonical Monte Carlo simulations have been published by Shi and Johnson [56], and experimentally by Wilson et al. [61], Talapatra, Rawat, and Migone [62], Bienfait et al. [63, 64], Jakubek and Simard [65], and Rols et al. [66]. The latter two experiments were for open SWNT bundles; the others were for closed SWNT bundles as were our simulations.

The quantity reported experimentally is not the specific heat itself, but a related observable, the isosteric heat $q_{st} = -\left[\frac{\partial (\ln P)}{\partial \beta}\right]_N = T^2 \left[\frac{\partial (\ln P)}{\partial T}\right]_N$. Experimentally one measures pressure changes in the sample chamber as the temperature is altered and infers the isosteric heat.

Computationally, isosteric heats are obtained from the differential heat of adsorption, $q_d = -\left(\frac{\partial E}{\partial N}\right)_T$, which itself is estimated by calculating system energies at fixed temperature for a range of particle numbers $N$ and performing a finite difference approximation to the derivative. The differential heat of adsorption is then related the isosteric heat by the relation $q_{st} = q_d + T$ [67, 68, 69, 70, 71].

Isosteric heat simulations and measurements by the aforementioned groups are compared with our results calculated using Metropolis Monte Carlo in Figure 2.6.
for closed SWNT bundles, and Figure 2.7 for open SWNT bundles. The scales of the figures for our results are not always the same as those for the experimental groups; they were adjusted to put our monolayer regime at a location in the plot corresponding to the experimentally estimated location of the monolayer. In theory these locations should be the same, but in practice the experimental samples do not have the exactly same geometry as our model, there are irregularities in the sample quality, and our model neglects the possibility of interstitial or within-tube adsorption, which alters the conversion from our particles adsorbed ($N$) to the experimentally measured coverage (Ar/C ratio or volume adsorbed).

The experimental results of Wilson et al. and Talapatra et al. for closed bundles disagree with our results, in particular obtaining much higher isosteric heats at low densities than we do, but they do agree with the heterogeneous bundle simulations of Shi and Johnson. Because our work agrees well with the homogeneous bundle simulations of Shi and Johnson, we attribute the discrepancy between the experimental groups and our simulations to bundle heterogeneity in their experiments and the lack thereof in our simulations. The small interstices within homogeneous bundles do not allow for adsorption; all the adsorption occurs on the exterior of the bundle. Heterogeneous bundles can have larger interstices that admit adatoms, providing additional opportunities for adsorption that increase the isosteric heat (Fig. 2.8).

By contrast, the experiments of Bienfait et al., Jakubek and Simard, and Rols et al. agree in magnitude with our simulations at low coverage. In light of the preceding discussion, this suggests that the bundles in their experimental samples were more homogeneous. However, this interpretation may be problematic, considering that there are limits on how homogeneous real bundles can be in practice; a “basin-hopping” optimization can be used to determine the dispersion in nanotube sizes [72, 73, 74], and the heterogeneous bundles simulated by Shi and Johnson are close to what this optimization predicts for realistic bundle dispersion.

In addition, even if their bundles were fully homogeneous, one might expect the isosteric heats of Jakubek and Simard and of Rols et al. to still be larger than ours at low coverage, since their bundles are open and allow for additional adsorption within the nanotubes themselves; because the binding energy of such sites is high, this adsorption is comparably favorable to groove adsorption [66].

These three experimental groups also measured a drop in isosteric heat at higher coverages approaching the monolayer, whereas our simulations found no such drop; our simulations may have not extended far enough past the onset of the monolayer to capture this feature. The drop in isosteric heat immediately after the groove phase is also more precipitous in our simulations than in the experimental data. The extended first plateau for the groove phase in the Rols et al. data is attributed by those authors to the extra adsorption within the open-ended SWNTs.

\footnote{See Sec. 2.4 for a discussion of why Metropolis MCMC was preferred over Wang-Landau MCMC for isosteric heat calculations.}
Figure 2.6.  The isosteric heat $q_{st} = -(\partial (\ln P)/\partial \beta)_N$ calculated in this work (left), compared to other work on closed SWNT bundles (right). The left figures are identical except for rescaling to match the right figures. Top right: open diamonds (squares) are from Shi and Johnson [56] simulations of heterogeneous (homogeneous) bundles at $T = 90$ K. Filled circles and triangles are from Wilson et al. [61] (near 90 K) and Talapatra et al. [62] (110–160 K at low coverage, 57–87 K at high coverage) experiments, respectively. Bottom right: Bienfait et al. [63] (77–96 K) experiments. [Sources: [56] (top right), [63] (bottom right).]

and so can be attributed to our assumption of closed SWNTs, but a gradual drop after the groove phase is present even in the Bienfait et al. data for closed SWNTs. Bundle heterogeneity could be an alternate explanation. A neglect of vaporization within the full experimental chamber volume may be one possible source of systematic error (Secs. 2.4, 2.5.6.2). Additional comparison of results may be found in Sec. 2.5.4.4.
Figure 2.7. The isosteric heat $q_{st} = -\left(\partial(\ln P)/\partial\beta\right)_N$ calculated in this work (left), compared to experiments with open SWNT bundles (right). The left figures are identical except for rescaling to match the right figures. Top right: Jakubek and Simard [65] (77–87 K) experiments (solid curve). Bottom right: Rols et al. [66] (77–90 K). [Sources: [65] (top right), [66] (bottom right).]

2.4 Limitations and future work

As discussed in the previous section, this work assumes that the bundles are homogeneous in nanotube size, which leads to disagreement with experimental results. Conceptually, it is not much more difficult to include heterogeneous bundles in the simulations; they are merely more computationally expensive, as the entire bundle must be simulated when the symmetry present in homogeneous bundles can no longer be applied (reducing the problem to that of a single groove site). A consideration of heterogeneous bundles would bring our work into closer agreement with experiment, as found in the Shi and Johnson heterogeneity study [56].

Above temperatures of 25–50 K, the effects of desorption become significant (Sec. 2.5.6.2). Our simulation cell is necessarily of very small volume close to the bundle surface where adsorption takes place, in order to restrict the computations
to a manageable number of particles. It neglects the existence of the vapor within the rest of the experimental chamber. Of course, real experiments measure the heat capacity of all of the gas within the chamber, not just the adsorbed gas on the surface. This causes experiments to measure a larger heat capacity than is reflected in our simulation, which may be responsible for some of the discrepancies between our work and experimental results (Secs. 2.3.4, 2.5.4.4).

Our simulations were purely classical, ignoring the effects of quantum mechanics. Back of the envelope calculations involving the quantum harmonic oscillator and the Debye phonon model suggest that quantum mechanics is significant below $T \approx 80$ K (Sec. 2.5.6.1). Since this is near the temperature of the first heat capacity peak (Fig. 2.4), those results may receive quantum corrections, but since the peaks are close to the temperature above which quantum effects become negligible, the corrections may not be large. The question can be resolved by appeal to quantum Monte Carlo methods, such as the path integral Monte Carlo algorithm (App. B.4).

The second peak in the heat capacity, associated with groove to monolayer promotion, is at a temperature not readily accessible to experiments with argon, due to the high vapor pressure required. Neon is a lighter gas, and with it higher temperatures could be reached within the physical constraints of the experimental apparatus. Our simulations could be repeated with neon instead of argon to make high-temperature predictions more accessible to experiment;\(^\text{13}\) conversely, the low

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\(^\text{13}\)Although the experimental accessibility of neon at high temperatures may not be as relevant
temperature predictions would be less relevant to experiment, because a lighter gas will remain quantum to higher temperatures. A study of neon in this system is currently in progress [75].

The Wang-Landau Monte Carlo algorithm proved very useful in calculating the temperature dependence of heat capacity. It was not used for calculating isosteric heats, and would be less useful in its existing form for that purpose. The main advantage of the Wang-Landau algorithm for heat capacities was its ability to estimate them at all temperatures simultaneously. However, isosteric heats are derived from the differential heat of adsorption, which is defined at fixed temperature, over a range of particle number. Thus, to calculate the isosteric heat, independent Wang-Landau simulations would have to be performed at each value of \( N \), just as Metropolis simulations would—except each Wang-Landau simulation would take longer than the corresponding Metropolis run at a single temperature because the Wang-Landau runs are calculating all temperatures.

Some of the benefit of the Wang-Landau algorithm would be recaptured if it were performed in the grand canonical ensemble instead of the canonical ensemble. With an estimate of the joint density of states \( g(E, N) \), the isosteric heat could be calculated directly—without finite differencing—from the grand partition function \( Q \), \( q_{st} = 1/\beta - (\partial Q / \partial \beta) / (Q \ln Q) \). A relatively straightforward extension of Wang-Landau Monte Carlo to the grand canonical ensemble has been investigated by Shell et al. [76]; a modification to the original Wang-Landau algorithm using kernel density estimation in place of energy binning was proposed by Zhou et al. [77]. The latter algorithm potentially leads to greater efficiency even in the canonical ensemble, and so could be applied in place of the algorithm used in this work (based on Shell et al.). (For a comparison of Wang-Landau variants for continuum systems, see Poulain et al [78].) Alternatively, the ensemble optimization broad-histogram technique of Trebst, Huse, and Troyer [79] may prove a more efficient alternative to any form of the Wang-Landau algorithm; Shell et al. have also proposed an improved method based on infinite temperature transition probabilities which may be combined with the original Wang-Landau algorithm [80].

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as one might think; although higher temperatures are accessible with neon, the features of interest in the argon heat capacity—such as the second peak—will occur at lower temperatures for neon due to its lower binding energy.
2.5 Article: “Thermodynamic properties and correlation functions of Ar films on the surface of a bundle of nanotubes”

Below is the text of the article Physical Review B 71, 245410 (2005) (DOI: 10.1103/PhysRevB.71.245410, arXiv: cond-mat/0412255) [60], ©2005 The American Physical Society, with minor corrections from the published version. See Sec. 2.5.7 for errata regarding the low density heat capacity and density of states, the applicability of the dimensional crossover model, and the accuracy of the volume density of states.

Thermodynamic properties and correlation functions of Ar films on the surface of a bundle of nanotubes

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Abstract

We employ canonical Monte Carlo simulations to explore the properties of an Ar film adsorbed on the external surface of a bundle of carbon nanotubes. The study is concerned primarily with three properties: specific heat \(c(T)\), differential heat of adsorption \(q_d\), and Ar-Ar correlation functions \(g(r)\). These measurable functions exhibit information about the dependence of film structure on coverage and temperature.

2.5.1 Introduction

Considerable interest has been attracted recently to the properties of simple gases (noble gases and small molecules) adsorbed near bundles of carbon nanotubes [81, 64, 63, 65, 82, 83, 62, 84, 85, 86, 61, 87, 88, 89, 90, 91, 92, 93]. This subject has been reviewed recently [88, 89]. The adsorption of these gases can occur within the tubes only if they are open, which is possible either during the process of nanotube formation (e.g., when endohedral C\(_{60}\) molecules are formed) [90], or after chemical treatment to open the tubes [91, 94]. The presence, or absence, of interstitial channel (IC) molecules is an open question in the case of an idealized bundle of identical tubes; there seems to be no doubt, however, that such IC adsorption occurs in laboratory samples of polydisperse tubes [56, 95, 96]. In contrast to variability in adsorption at these sites, the adsorption of gas on the
external surface of the bundle is a ubiquitous phenomenon, in which the film coverage increases with the pressure \( P \) of the coexisting gas. In that exohedral environment, an adatom is strongly attracted to the groove region between two neighboring tubes; there, the film forms a quasi-one-dimensional phase. Further adsorption at low temperature \( T \) is predicted to manifest a so-called three-stripe phase of gas aligned parallel to the grooves \([59, 97, 98]\). At higher gas coverage \( N \), there occurs a two-dimensional monolayer phase, qualitatively analogous to that found on the graphite surface \([99, 1, 6.1.4]\). At even higher coverage, a multilayer film grows as \( P \) increases. There is an upper limit of total film coverage, set by the bundle’s curvature \([100, 101]\); this limit has yet to be explored.

This study extends a previous investigation \([102]\) of the adsorption of Ar gas on the external surface of a nanotube bundle. Argon was chosen as a model adsorbate because its gas-gas interaction is well known, making it a standard fluid in the study of simple fluids. In the previous study, denoted I, we employed the grand canonical Monte Carlo simulation method to explore the evolution of the equilibrium film as a function of \( P \) and \( T \). The present paper, stimulated by recent and proposed experiments, adds three results to those derived in the previous study. One property is the specific heat, \( c(T) \), which is computed here from energy fluctuations, evaluated using simulations within the canonical ensemble. The second property is the differential heat of adsorption, \( q_d = -(\partial E/\partial N)_T \), where \( E \) is the energy of the film. This quantity is closely related to another quantity, which is more often measured experimentally, the isosteric heat \( q_{st} = -(\partial(\ln P)/\partial \beta)_N \) [where \( \beta = 1/(k_B T) \)], by the relation \([67]\) \( q_{st} = q_d + k_B T \) (assuming an ideal gas coexisting with the film). The third property reported here is the anisotropic correlation function of the overlayer. This quantity is related by Fourier transform to results of diffraction experiments. With the exception of the isosteric heat calculated by Shi and Johnson \([56]\), none of these properties has been explored in simulation studies of films on nanotube bundles, prior to the present work.

The outline of this paper is the following. Section 2.5.2 summarizes our simulation methods. Section 2.5.3 reports results for the density and correlation functions. Section 2.5.4 presents results for the thermodynamic properties, \( c \) and \( q_d \). Section 2.5.5 summarizes our results.

### 2.5.2 Computational methods

When not explicitly contradicted in this paper, it may be assumed that the physical system and computational method are as described in I. The primary model system is a bundle of infinitely long, cylindrically symmetric carbon nanotubes of identical radii equal to 6.9 Å. Only two adjacent nanotubes on the external surface of the bundle are simulated. The \( y \) axis is parallel to the nanotubes, and the \( z \) axis is directed away from the surface of the bundle. Periodic boundary conditions are imposed in the \( x \) and \( y \) directions (approximating the surface of the bundle as an
infinite plane of nanotubes); reflecting boundary conditions are imposed in the $z$ direction. The unit simulation cell, whose volume contains half of each of the two adjacent nanotubes with the groove in between them at the center, is 17 Å in the $x$ direction, 34 Å in the $y$ direction, and 40 Å in the $z$ direction.

The simulations were done in the canonical ensemble, rather than the grand canonical ensemble more commonly used in adsorption simulations, in order to facilitate the calculation of the heat capacity. Two Markov Chain Monte Carlo simulation methods were used, the Metropolis algorithm [103, 53] and the Wang-Landau algorithm [104, 105, 106]. The Metropolis algorithm was used to calculate configurational observables, such as density distributions and correlation functions. The Wang-Landau algorithm was used to calculate thermodynamic observables expressible in terms of ensemble averages or their derivatives, such as specific and isosteric heat, for certain $N$; the Metropolis algorithm was used to determine the full $N$ dependence.

The Metropolis algorithm proposes new configurations and accepts them with a probability equal to $\min\{1, P(x')/P(x)\}$, where $P(x)$ and $P(x')$ are the probabilities of the old and new configurations $x$ and $x'$; this acceptance rule causes the random walk to converge to the probability distribution $P(x)$. By choosing $P(x)$ proportional to the Boltzmann factor $\exp(-\beta U(x))$, where $U(x)$ is the potential energy of the configuration, the Metropolis algorithm uniformly samples configuration space. For the Metropolis simulations of each $(N, T)$, $4 \times 10^7$ Monte Carlo moves were discarded during the initial equilibration to converge the algorithm to the Boltzmann distribution, then $4 \times 10^6$ moves were generated, from which $10^4$ samples were drawn to perform simulated measurements of system observables.

The Wang-Landau algorithm, like the Metropolis algorithm, also proposes and accepts configurations with a probability equal to $\min\{1, P(x')/P(x)\}$. However, it chooses $P(x)$ to be proportional to $P[U(x)] = 1/g[U(x)]$, where $g(U)$ is the (relative) density of states, thus uniformly sampling energy space (instead of configuration space, as in the Metropolis algorithm). It dynamically refines its estimate of the density of states by counting each visit to a state of a given energy $U$ (or, rather, within a small range of energies $U \in [U_i - \epsilon/2, U_i + \epsilon/2]$ about an energy bin $U_i$ of width $\epsilon$), and multiplies its running estimate of $g(U_i)$ by a constant factor $f$. It continues the random walk until each energy is visited approximately uniformly (a “flat histogram” of visits in energy space), whereupon it reduces the factor $f \rightarrow f^{1/2}$ and starts another iteration. The algorithm terminates when $f$ is reduced to a preset minimum greater than unity, with values closer to unity yielding more accurate estimates of the density of states.

Once an estimate of $g(U)$ is produced, it can be used to calculate the partition function directly

$$Z \sim \int dx e^{-\beta U(x)} \approx \sum_i g(U_i)e^{-\beta U_i}.$$  \hspace{1cm} (2.4)

Thermodynamic quantities can then be calculated from the partition function, as
usual. One advantage of the Wang-Landau algorithm over the Metropolis algorithm (and the main reason for using it for this study) is that, because temperature dependence appears only in the Boltzmann weight \( \exp(-\beta U) \) and not in the density of states \( g(U) \) itself, a single simulation of \( g(U) \) can calculate thermodynamic observables for all temperatures at once.

Some modifications and improvements to the original published Wang-Landau algorithm were implemented. Boundary effects were properly handled \([107]\). To adapt the original lattice-based algorithm to continuum systems, preliminary Metropolis runs at low temperature were performed to estimate a lower bound on the energy bins (i.e., the ground state energy) \([76]\). The simulation can also become trapped for long periods of time in regions of high degeneracy, so that energies with small \( g(U) \) go a long time before being revisited. To remedy this, the energy bins can be broken up into overlapping subranges; ergodicity can be achieved more rapidly if the interval of energies to be traversed is smaller. Separate simulations are performed in each subrange, producing independent estimates of \( g(U) \). Some care must be taken in combining them into an estimate of \( g(U) \) over the full energy range: because each simulation calculates only the relative density of states, the estimates will not generally match up at the boundaries of the subranges. To overcome this, each subrange estimate of \( g(U) \) is rescaled by a constant factor that minimizes the least-square error in \( \log g(U) \) wherever two neighboring subranges overlap in energy \([76]\). This corresponds to choosing normalizing factors \( C_n \) that minimize the sum \( \sum_i \{ \log [g_n(U_i)/C_n] - \log [g_{n-1}(U_i)] \}^2 \) over the overlapping bins \( U_i \) (where \( g_n \) denotes the density of states simulated over subrange \( n \)), and then rescaling \( g_n(U) \) by \( C_n \).

For the Wang-Landau simulations of each \( N \), 1500 equal-sized energy bins were used in a range \([U_{\text{min}},0]\), where \( U_{\text{min}} \) is the ground state energy. The 1500 bins were divided into four overlapping subranges, simulated separately, consisting of the bins numbered 1–150, 76–787, 713–1425, and 1351–1500. A histogram was considered “flat” when the number of visits to any particular energy bin was less than \( \pm 20\% \) the average number of visits to any bin. The minimum \( f \) factor was \( f_{\text{min}} = 1 + 10^{-5} \).

### 2.5.3 Correlation functions

For the purposes of this paper, the three-dimensional pair correlation function is defined as the probability density \( g(\mathbf{r}) \) that two particles are separated by a relative displacement \( \mathbf{r} \). Its projection \( G(x, y) \equiv \int dz \, g(\mathbf{r}) \) into the \( xy \) plane is depicted in Fig. 2.9. The contours become wider and more irregular at higher temperatures, as the particles are thermally excited out of their well-defined low temperature sites.

In the top pair of panels, one observes the nearly periodic, quasi-one-dimensional (1D) order within the groove. As studied recently in connection to nanotube
Figure 2.9. Equiprobability contour plots of the projection into the $xy$ plane of the pair correlation function, $G(x, y)$ for, from top to bottom, $N = 9$ (groove), $N = 18$, $N = 27$ (three-stripe), and $N = 54$ (monolayer), at $T = 60$ K (left) and $T = 90$ K (right). Distances are in angstroms. Note that the vertical axis scale is compressed relative to the horizontal.

adsorption [108, 109, 110, 111, 112, 113], this phase may undergo a phase transition due to the weak interactions between particles in neighboring grooves. In the second pair of panels, one observes that the correlations within the three-stripe phase are weaker and even more $T$ dependent than those in the groove phase. At 90 K, at higher coverage (seen in the middle four panels), the stripes are not as straight, primarily due to transverse excitation (as discussed in Sec. 2.5.4.3). Note that the half-filled stripe case ($N = 18$) is somewhat less ordered than the completely filled three-stripe case ($N = 27$), as is expected. The bottom panels of Fig. 2.9 exhibit
a highly correlated anisotropic two-dimensional (2D) solid at 60 K, the order of which washes out nearly completely by 90 K, as the monolayer melts.

Previous experimental studies of Ar adsorption onto planar graphite [114, 115, 116, 117] found that the melting temperature depends on density, starting near 55 K at low density, and increasing with density. Although the system studied here differs from that experiment in geometry, we expect the melting temperature of the monolayer in our system to similarly increase with density. The corrugation of the nanotube bundle should elevate the melting temperature somewhat compared to a planar surface, as the grooves will serve to more strongly confine the film’s structure.

Bienfait et al. have measured diffraction patterns for Ar on nanotube bundles [64]. Probably due to heterogeneity (for which there exists evidence in bare surface diffraction), the diffraction data are not easily interpreted. There is, however, definite evidence of 1D interatomic spacing (i.e., a peak at wave vector $q = 17/\text{nm}$) at low coverage and 2D close-packed spacing (peak near 20/\text{nm}).

### 2.5.4 Heat capacity

#### 2.5.4.1 Overview

The isochoric specific heat, $c(T) = (\partial E/\partial T)_V/N$, i.e., the heat capacity (per particle) at constant volume, was calculated from ensemble averages. It is known [118] (§3.6) that the heat capacity can be given in terms of energy fluctuations, $(\partial E/\partial T)_V = (\langle E^2 \rangle - \langle E \rangle^2)/(k_B T^2)$, where $\langle \cdot \rangle$ denotes an expectation taken over the canonical ensemble. The equipartition theorem gives the kinetic energy contribution of $\frac{1}{2}k_B$ per degree of freedom to the specific heat, yielding a total $c(T) = \frac{3}{2}k_B + (\langle U^2 \rangle - \langle U \rangle^2)/(N k_B T^2)$. Given the density of states $g(U)$ calculated with the Wang-Landau algorithm, the expectations may be calculated from $\langle U \rangle = Z^{-1} \sum_i [U_i g(U_i) \times \exp(-\beta U_i)]$, and similarly for $\langle U^2 \rangle$. The heat capacity was also estimated directly from the derivative $(\partial E/\partial T)_V$ by means of a finite difference approximation. These latter estimates, while consistent with the fluctuation estimates, were “noisier” and are not considered further in this paper.

The simulated $c(T)$ for the groove, three-stripe, and monolayer phases is shown in Fig. 2.10. Note that the overall trend is for $c(T)$ to have a remarkably high value, in the range 3–7 Boltzmanns, much higher than might be expected from simple quasi-one-dimensional and two-dimensional models. We do not have a detailed quantitative model to explain all of the observed features, but we can give a qualitative explanation of its behavior. The explanations are justified by examining the probabilities of finding particles at given energies in the external potential, Fig. 2.11, indicating the fraction of particles that are in the groove, stripes/monolayer, etc. (quantified in Table 2.1).
2.5.4.2 Low density

Consider first the low-density limit [119]. At low temperatures, the specific heat is near 2.5 Boltzmanns. This is to be expected: the three kinetic degrees of freedom each contribute the usual 1/2 Boltzmann; the two transverse dimensions, for which the external potential is approximately harmonic at its minimum at the center of the groove, each contribute another 1/2 Boltzmann. As the temperature increases, a peak in the specific heat occurs near 170 K when substantial numbers of adatoms are promoted out of the groove and into monolayer sites elsewhere on the surface of the nanotubes (see Table 2.1). As $T \to \infty$, the adatoms desorb from the surface altogether, and $c(T)$ approaches the 3/2 Boltzmanns of the three kinetic degrees of freedom of a pure vapor. (This will be the case for all other densities as well, in the high-$T$ limit.)

These conclusions are corroborated, as mentioned, in the first row of Fig. 2.11; these results, in the low-density limit, can also be understood by examining the
so-called “volume density of states” [120] \( f(U) \), defined such that \( f(U) \, dU \) is the volume of space bounded by infinitesimally separated isopotential surfaces, \( U < U_{\text{ext}} < U + dU \). This function is related to the energy probability density \( P(U) \) in Fig. 2.11 at low density by \( P(U) = \rho f(U) \exp(-\beta U) \), where \( \rho \) is the number density of particles. By dividing an estimate of \( P(U) \) at a given temperature (here, \( T = 300 \) K) by the exponential Boltzmann factor, we obtain an estimate proportional to the volume density of states \( f(U) \), depicted in Fig. 2.12.

The qualitative form of this figure can be explained by appealing to a previously studied analytic model, the dimensional crossover model [119]. This exactly soluble model ignores interparticle interactions (an assumption appropriate for the low-density limit) and treats the nanotube bundle as consisting solely of two regions, a one-dimensional groove region approximated by a harmonic potential in
Table 2.1. Percentage of particles in the groove \((-1600 \, \text{K} < U_{\text{ext}} < -1200 \, \text{K})\), monolayer \((-1200 \, \text{K} < U_{\text{ext}} < -400 \, \text{K})\), and vapor \((U_{\text{ext}} > -400 \, \text{K})\) regimes, for the low-density limit \((N = 1)\), and the groove \((N = 9)\), three-stripe \((N = 27)\), and monolayer \((N = 54)\) phases, for various temperatures.

<table>
<thead>
<tr>
<th>(N)</th>
<th>(T , (\text{K}))</th>
<th>% groove</th>
<th>% monolayer</th>
<th>% vapor</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20</td>
<td>100</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>170</td>
<td>61</td>
<td>31</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>14</td>
<td>35</td>
<td>51</td>
</tr>
<tr>
<td>9</td>
<td>20</td>
<td>100</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>93</td>
<td>6</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>175</td>
<td>43</td>
<td>42</td>
<td>15</td>
</tr>
<tr>
<td>27</td>
<td>20</td>
<td>33</td>
<td>67</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>55</td>
<td>33</td>
<td>67</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>165</td>
<td>22</td>
<td>60</td>
<td>18</td>
</tr>
<tr>
<td>54</td>
<td>20</td>
<td>17</td>
<td>83</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>17</td>
<td>77</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>140</td>
<td>14</td>
<td>54</td>
<td>32</td>
</tr>
</tbody>
</table>

The two transverse dimensions, and a two-dimensional planar monolayer region approximated by a harmonic potential normal to the surface. Evaporation from the monolayer to vapor is neglected. Its (configurational) partition function is given by

\[
Z_{\text{crossover}} = \int_{\text{groove}} d^2r \, e^{-\beta(V_g + \frac{1}{2} \alpha r^2)} + L_s \int_{\text{mono}} dz \, e^{-\beta(V_m + \frac{1}{2} k_m z^2)},
\]

where the parameters \(V_g = -1671 \, \text{K}\), \(\alpha = 4898 \, \text{K/Å}^2\), \(V_m = -853 \, \text{K}\), and \(k_m = 4792 \, \text{K/Å}^2\) were determined by a fit to the external potential, \(L_s = 18 \, \text{Å}\) is the approximate width of the monolayer region in the transverse direction, and integrations were taken over regions extending 2 Å away from the groove minimum and 1 Å away from the monolayer minimum.

For the low energies dominated by the groove phase, the crossover model approximates the external potential as \(U = V_g + \frac{1}{2} \alpha r^2\). The cylindrical volume enclosed by an isopotential goes like \(V \sim r^2\), and \(f(U) = dV/dU = (dV/dr)/(dU/dr)\), which is a constant; indeed, the \(f(U)\) calculated in Fig. 2.12 is nearly constant at low energies. For the monolayer region, close to the potential minimum, \(U = V_m + \frac{1}{2} k_m z^2\). The rectangular volume enclosed by an isopotential goes like \(V \sim z\), and \(f(U) = (dV/dz)/(dU/dz)\), which goes like \(z^{-1} \sim (U - V_m)^{-1/2}\) for \(U > V_m\). This divergence in the model accounts qualitatively for the peak in \(f(U)\) just above the monolayer energy of about \(-800 \, \text{K}\). For high energies dominated by the vapor phase, we can treat the substrate as a semi-infinite rectangular volume, and
approximate the external potential by a long-distance \( (r^{-6}) \) Lennard-Jones potential integrated over this region, which yields \( U \sim -z^{-3} \). Then \( f(U) \) will go like \( z^{-4} \sim (-U)^{-4/3} \), qualitatively accounting for the sharp rise in \( f(U) \) as \( U \to 0 \).

Given the volume density of states \( f(U) \), we can then obtain the energy probability density \( P(U) \) at any other temperature by scaling this temperature independent function by the appropriate Boltzmann weight. In particular, the three columns of the first row of Fig. 2.11 are just the function in Fig. 2.12 scaled by Boltzmann factors \( \exp(-\beta U) \) that decay with decreasing rapidity as \( T \) increases (\( \beta \) decreases). The groove is highly populated at low temperatures (large \( \beta \)) when the exponential damping is great enough to suppress population at higher energies. The monolayer becomes populated at intermediate temperatures when the damping is no longer sufficient to suppress the peak in \( f(U) \) that occurs at the monolayer energy \( (-800 \text{ K}) \), and the vapor becomes populated at still higher temperatures (small \( \beta \)) when the damping fails to suppress the rapid increase in \( f(U) \) towards 0 K.

The partition function of the crossover model can also be used to calculate the specific heat directly. As seen in Fig. 2.10, the correspondence between the
prediction of this analytic approximate model and the simulated full model is quite good.

2.5.4.3 Higher coverage

Next, consider the groove phase. At low temperatures, the specific heat is near 3 Boltzmanns. A contribution of 2.5 Boltzmanns is accounted for by the same argument as for the low density limit. Unlike the low density limit, however, the groove phase is densely packed with adatoms, and interparticle interactions must be considered. An additional 1/2 Boltzmann arises from confinement in the longitudinal dimension, for which the Ar-Ar interaction potential is approximately harmonic at its minimum when the adatoms are stably distributed in equilibrium. As the temperature increases, evaporation out of the groove begins. At \( T \approx 70 \) K, evaporation is great enough to excite adatoms out of the groove; while not many of these atoms reach the monolayer region (Table 2.1), there is still a large change in potential energy for a small increase in temperature, and thus a large specific heat. The specific heat then decreases slightly with increasing temperature, since the change in energy is not as large once the initial adatoms have begun to be promoted. This low-temperature peak is not present in the low-density case because, as seen in both Table 2.1 and Fig. 2.9, the adatoms are not spread transversely as greatly about the immediate groove region at low temperatures in the low-density case as they are in the groove case. However, in a manner qualitatively analogous to the low-density limit, an additional, larger peak in the specific heat is found at still higher temperatures (\( T \approx 175 \) K), mostly from promotion from the groove into the stripes and the rest of the monolayer.

Like the groove phase, the three-stripe phase starts out at 3 Boltzmanns at low temperatures, similar to the groove phase, except that the 1 Boltzmann from external potential confinement in the transverse plane is replaced by 1/2 Boltzmann from external potential confinement normal to the surface, and 1/2 Boltzmann from interparticle confinement along the surface in the transverse plane. The specific heat peaks near \( T = 55 \) K; this is not due to a significant fraction of particles being promoted from the groove to the stripes, as one might expect, but rather to a wider range of energies within the stripe/monolayer region, and promotion from the stripes to the rest of the monolayer; see Fig. 2.11 and Table 2.1. It peaks again near \( T = 165 \) K, with as the groove empties into the stripes and monolayer, as well as the beginning of evaporation off the surface.

The monolayer phase also starts out at 3 Boltzmanns at low temperatures, for reasons analogous to the three-stripe phase. At higher temperatures, there is a peak in the specific heat near \( T = 80 \) K which, like the three-stripe peak, is largely due to a broadening of the particles across a range of energies in the monolayer region, as well as some promotion from the monolayer to the bilayer (Fig. 2.11). Another peak appears near \( T = 140 \) K, corresponding to evaporation out of the
monolayer into the bilayer, and to vapor.

2.5.4.4 Further results

The $N$ dependence of several isotherms is displayed in Fig. 2.13. Of particular note is the rapid rise in the specific heat near $N \sim 8$, just before groove completion, as $T$ goes from 60 to 90 K. This is attributed to promotion out of the groove. Similarly, near monolayer completion the marked increase in $c$ with $T$ is attributed to thermal promotion out of the monolayer.

![Figure 2.13](image)

**Figure 2.13.** The dimensionless specific heat $c(N)/k_B$ as a function of density, at $T = 60$, 75, and 90 K.

It is also illuminating to study the differential heat of adsorption, $q_d(N) = -(\partial E/\partial N)_T$, the energy required to adsorb an additional particle onto the surface at constant temperature. The differential heat is related to the heat capacity at constant density, $C_N = (\partial E/\partial T)_N$, by a Maxwell relation derived from the total derivative $dE = (\partial E/\partial T)_N dT + (\partial E/\partial N)_T dN$, which yields

$$
\left( \frac{\partial C_N}{\partial N} \right)_T = - \left( \frac{\partial q_d}{\partial T} \right)_N .
$$

(2.6)
The differential heat of adsorption is summarized in Fig. 2.14. At low densities, the differential heat is near the minimum of the external groove potential $\approx -1600 \text{ K}$, becoming slightly larger at lower temperatures. Both this value and the $T$ dependence at low $N$ can be understood from the low-density equation of state, $U/N = V_g + \frac{5}{2} k_B T$. As additional particles are added, the energy for each additional particle is reduced by slightly more than this amount, to include the interaction energy. As the groove phase is approached, the groove becomes tightly packed and the interaction energy becomes significant, so that adding an additional particle reduces the energy by the external groove potential plus the Lennard-Jones well depth, $\epsilon \approx -120 \text{ K}$ for Ar. The difference in $q_d(N)$ between low and high temperatures is particularly large just before the groove phase, which in accordance with Eq. (2.6) corresponds to the steepest increase in heat capacity as seen in Fig. 2.13; at the $N = 9$ groove phase itself, where the heat capacity peaks with increasing $N$, we see correspondingly little difference in the differential heat at various temperatures. At the other extreme, near monolayer completion, a similar $T$ dependence is observed. The large decrease in $q_d$ with increasing $T$ is consistent with Eq. (2.6) and Fig. 2.13; the latter shows a large value of $dC/dN$ except below 60 K. The explanation is monolayer-to-bilayer promotion above 60 K.

Experimental measurements of isosteric heat for argon on nanotube bundles have been reported by Wilson et al. [61], Talapatra, Rawat, and Migone [62], Jakubek and Simard [65], and Bienfait et al. [64, 63]; grand canonical Monte Carlo simulations have been published by Shi and Johnson [56].

The isosteric heat calculations of Shi and Johnson for adsorption of Ar on a homogeneous bundle at 90 K agree closely with our results, with a peak of $q_{st} = 14 \text{ kJ/mol}$ just before the groove phase, corresponding to our peak of 1650 K. Past the groove phase, their calculated isosteric heat drops and remains constant with coverage, slightly below 10 kJ/mol, corresponding to our nearly constant value near 1200 K.

Shi and Johnson compared their calculations to the experimental results of Wilson et al. and Talapatra et al., and since we agree with those calculations, we will briefly summarize their conclusions. Our calculations agree with both experiments at higher coverage, beginning at the three-stripe phase, but their isosteric heats at lower coverage are dramatically greater than ours, as large as 18 kJ/mol ($\sim 2200 \text{ K}$) at low coverage. We ascribe this discrepancy with experiment to our neglect of bundle heterogeneity, following Shi and Johnson, whose simulations of heterogeneous bundles agreed well with both experiments.

In contrast, the isosteric heats measured by Jakubek and Simard agreed well with our simulations, with a peak of 137 meV ($\sim 1600 \text{ K}$) near the groove, descending to plateau of 106 meV ($\sim 1200 \text{ K}$) through to monolayer coverage. This agreement with our calculations suggests that their bundles were more homogeneous than those studied in the other two experiments. It should be noted, how-
ever, that their isosteric heat continues to decrease as coverage increases, whereas our isosteric heat appears to rise slightly as the monolayer is approached. The isosteric heat of Wilson et al. also drops past the monolayer.

Like the other experiments, the results of Bienfait et al. for Ar exhibit two plateaus in the dependence of the isosteric heat on coverage. The lowest coverage data yield $q_{st} = 15$ kJ/mol, or about 1800 K. Our predicted value in this range is of order 1650 K. The higher coverage, broad plateau corresponds to a measured $q_{st} = 1200$ K, which agrees well with the value we find for the three-stripe phase. However, the data at monolayer coverage continue to decrease, while ours appear to increase, as noted. Another area of disagreement is the extent, in coverage, of these plateaus. In the data, the second plateau extends over a coverage range comparable to that of the first plateau. Our calculations, instead, find that groove region of high $q_{st}$ extends over just one-sixth of the range of the combined three-stripe plus monolayer regime (grouped together because of similar values of $q_{st}$). This discrepancy may be attributed to the role of large interstitial cavities within the bundle, as argued by Bienfait et al.
2.5.5 Summary and conclusions

Our results are intended to stimulate further experimental studies of this system and analogous systems involving other gases on nanotube bundles. We have investigated the variation of thermodynamic properties with $T$ and $N$. One of the more interesting general results is that the specific heat is typically larger than might have been expected from either simple models used to treat these systems (either independent particles or a solid) [93] or from experimental results for films on graphite [99]. For most conditions studied here, the specific heat exceeds three Boltzmanns, with average values in the range four to five Boltzmanns. In contrast, the specific heat of independent particles [119] in this environment is less than three Boltzmanns, except at high $T$ (above 100 K), when the particles are excited out of the groove. The large values found in these simulations arise from the fact that the highly corrugated potential surface presents a sequence of excitation steps (groove→three-stripe→monolayer→⋯→vapor), each of which enhances the specific heat.

The temperature dependence of the specific heat shows a characteristic double-peak structure. All densities show a large peak near 175 K, corresponding to promotion of adatoms out of the groove into the monolayer region. The groove, three-stripe, and monolayer phases show an additional peak at lower temperature, corresponding to a thermal broadening in the range of external potential energies of the particles, rather than to any significant promotion of particles into qualitatively different regions.

Other principal results involve the relation between the evolution of film structure (with increasing $N$) and the corresponding thermodynamic and correlation functions. As the groove begins to fill ($N$ approaching 9), the heat capacity shows a dramatic jump as a function of coverage. Consistent with the Maxwell relation, Eq. (2.6), the differential heat decreases with $T$ at that point (Fig. 2.14). Analogous behavior occurs near completion of the three-stripe phase, near $N = 27$.

Our study has been fully classical, but the temperatures beneath which quantum effects become significant can be estimated [119]. We estimate that quantum effects can be ignored above about 80 K (see Sec. 2.5.6.1). This is a higher temperature than some of the important structure in the heat capacity—the first peak in the heat capacity occurs at or below this temperature. Modifications to the heat capacity from quantum mechanics at very low energies are given by Debye theory [93, 121, 122, 123]: we expect that $c(T) \rightarrow 0$ as $T \rightarrow 0$, and $c(T) \propto T^d$, where $d \sim 1$ for the groove and $d \sim 2$ for the monolayer, if the density is high enough to form a bulk phase. To evaluate quantum effects accurately would require application of the path integral Monte Carlo method to the problem [124].

We note, also, that an experimental heat capacity cell has a volume on the order of 1–10 cm$^3$, whereas our simulation volume was on the order of $10^{-20}$ cm$^3$. Our simulation, focusing on small volume nearer the adsorbed film, thus ignores almost all of the volume in which desorption into vapor can occur. This causes
the simulation to underestimate the heat capacity that will be experimentally measured. The effects of desorption cannot be ignored when the number of atoms in the vapor starts to approach the number of atoms in the film; this occurs at roughly 25–50 K (see Sec. 2.5.6.2).

Particularly interesting results from the correlation function studies include the reduced longitudinal correlations in the groove and striped phases as $T$ rises above 60 K. These results would be amenable to testing by diffraction experiments even if the samples included a randomly oriented batch of nanotubes; this is a familiar problem dealt with in powder averaging of small-sample experiments.

This paper studied a system of identical nanotubes. The sensitivity of $c(T)$ to nanotube heterogeneity, with an asymmetric groove region between nanotubes of different sizes, is a potentially interesting subject for future investigation [56, 95, 96].

Acknowledgments

We are very grateful to David Goodstein for a helpful explanation of the thermodynamics of adsorption, to Oscar Vilches for a discussion of experimental issues, to Mary J. Bojan for discussions of the simulation methods and their interpretation, and to Michel Bienfait for his helpful comments. This work was supported by the National Science Foundation.

2.5.6 Appendix

2.5.6.1 Quantum effects

The upper bound on the temperature at which quantum effects must be considered is dominated by the physics of the deepest energy well, i.e., the groove. We can obtain one estimate by considering the minimum energy of longitudinal phonons in the groove in Debye theory, $\hbar \omega_D$, where $\omega_D = \sqrt{k/m}$ and $k = 28^3/3(9\epsilon/\sigma^2)$ is the force constant of a quadratic approximation to the minimum of the Ar-Ar interaction potential, a 12-6 Lennard-Jones potential $U_{\text{int}} = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$, with $\sigma = 3.4$ Å, $\epsilon = 120$ K for Ar. The corresponding energy is 27 K. This estimate considers only Ar-Ar interactions and ignores the external potential; we can obtain a complementary estimate by ignoring the interactions and considering only the external potential. We return to the crossover model of the groove, outlined in Sec. 2.5.4, as a two-dimensional harmonic oscillator with a force constant $\alpha = 4898$ K/Å$^2$. Treating it now as a quantum harmonic oscillator, it is excited at an energy $\hbar \omega_\perp$, where $\omega_\perp = \sqrt{\alpha/m}$ and $m$ is the atomic mass of argon. The corresponding energy of this second estimate is 77 K. Taking the larger of the two as a conservative estimate, we expect that quantum effects can be ignored above about 80 K.
2.5.6.2 Effects of desorption

We can estimate the temperature at which desorption into the full volume of an experimental cell becomes significant, by determining when the ratio $N_v/N_m$ of atoms in the vapor to atoms in the monolayer becomes significant. Extending the crossover model, we can consider the monolayer and vapor phases as separate systems, the monolayer modeled as a surface with a harmonic normal potential, and the vapor modeled as a free gas. The ratio $N_v/N_m$ is then given by the ratio of their respective partition functions

$$\frac{N_v}{N_m} = \frac{\int dz}{\int_{mono} dz} e^{-\beta[V_m+(1/2)k_m z^2]}.$$  

(2.7)

We take the first integral between zero and the cell height, $h$; the second integral may be safely taken between zero and $\infty$, in the interests of finding an analytic solution. This gives

$$\frac{N_v}{N_m} = \frac{h}{\sqrt{\pi/(2\beta k_m)}} e^{-\beta V_m}.$$  

(2.8)

The fraction of atoms in the vapor above which desorption should be considered “significant” is ambiguous, but we might take it to be 10%–20%. Solving Eq. (2.8) for $\beta$, using $h = 1$ cm and the values for $V_m$ and $k_m$ found in Sec. 2.5.4.2, this corresponds to a temperature in the range of 25–50 K.

This calculation neglects interparticle interactions. Their inclusion would lower the estimate of the temperature at which desorption from the monolayer into vapor becomes significant, analogously to how the evaporation from the groove to the monolayer takes place at a lower temperature when the groove is packed—the interacting case—than when it is sparsely populated and the adatoms are effectively noninteracting. This is supported by the data in Table 2.1: more groove→monolayer promotion occurs for $N = 9$ at $T = 175$ K than for $N = 1$ at the comparable temperature $T = 170$ K, indicating that the groove promotion begins at a lower temperatures for the interacting $N = 9$ than for the noninteracting $N = 1$.

2.5.7 Errata

Since the publication of this article [60], some errors have come to light. Due to improperly chosen overlapping energy ranges, the Wang-Landau algorithm underestimated the density of states at high energies (near $U = 0$) for the low density ($N = 1$) case. This led to a corresponding underestimate of the magnitude of the heat capacity peak which puts the heat capacity in disagreement with the dimensional crossover model (Sec. 2.5.4.2). In addition, the method used for calculating the volume density of states (Fig. 2.12) was numerically inaccurate, and has been superseded by a Wang-Landau estimate. These points are treated in more detail below.
2.5.7.1 Wang-Landau density of states and heat capacities

As discussed in Sec. 2.5.2, the density of states was estimated by combining four runs of the Wang-Landau algorithm over overlapping energy ranges. It was necessary to divide the energy into subranges in order to facilitate simulation ergodicity. Low energies required their own simulation because there are few low-energy states, so a simulation encompassing the full energy range would rarely visit them, even with the Wang-Landau biased random walk which favors rarely visited states. If the low energies have their own devoted simulation, on the other hand, then the simulation can spend all of its time exploring that energy range. The subranges for the independent simulations must overlap so that the simulated relative densities of states, which have different normalization constants, may be matched across the boundaries of the subranges.

For the work in this article, the full range of energies (up to $U = 0$) was divided into 1500 energy bins, which were themselves divided into four overlapping subranges, simulated separately, consisting of the bins numbered 1–150, 76–787, 713–1425, and 1351–1500. The logarithm of the density of states was depicted in Fig. 2.3, but the $N = 1$ curve is barely visible on that scale. An enlarged plot of the exponential of that curve (along with other curves to be discussed shortly), which served as the basis for the heat capacity results published in this article, is given in Figure 2.15.

As is visible in that figure, the density of states computed by the Wang-Landau algorithm for four overlapping subranges is erratic for $U > -200$ K. This is due to the simulated densities of states in the upper two energy ranges not adequately overlapping. This discrepancy was originally overlooked in light of the apparent agreement of the resulting $N = 1$ heat capacity curve with both the dimensional crossover model (Fig. 2.10) and with independent Metropolis simulations (Fig. 2.5).

This problem can be solved by merging the two upper ranges, giving three energy subranges: bins 1–150, 76–787, and 713–1500. Creating a small subrange at high energies (bins 1351–1500) was unnecessary to begin with because, unlike the necessary subrange at low energies (bins 1–150), there is no ergodicity problem at high energies: they are plentiful and the simulation visits them often.

The result of the Wang-Landau simulations for $N = 1$ with three energy ranges is also depicted in Fig. 2.15. It does not suffer the erratic behavior of the four-range simulations at high energies ($U \approx 0$), but is otherwise in close agreement with the four-range results.\textsuperscript{14} Because the four-range simulations underestimated the true density of states at high energies, the heat capacity is also underestimated.

Figure 2.16 compares the new three-range heat capacities to the published four-range results as well as to the dimensional crossover model. The heat capacity peaks are located approximately at the same temperatures, but the magnitude

\textsuperscript{14}Thanks to Daniel Shai for pointing out the discrepancy between the three-range and four-range results.
Figure 2.15. Configurational density of states in the low density \((N = 1)\) adsorption phase, from Wang-Landau simulation calculated using three and four overlapping energy subranges (the latter used in [60]); as well as the volume density of states, calculated using Boltzmann weighting of the particle energy distribution and by the volume grid histogram method (the latter used in [60]). [The volume grid histogram data are due to Daniel Shai.]

of the three-range heat capacity at its peak is roughly 40% larger than the (four-range) results published in this article. This is somewhat puzzling, as the density of states was only underestimated at energies near the vaporization energy (0 K), so one might expect the underestimation of the heat capacity to be most significant at high temperatures. Instead, the heat capacity was most underestimated at temperatures corresponding to the onset of groove-to-monolayer promotion (characterized by the density of states near \(U = -800\) K).

The corrected results put the simulation low density heat capacities in disagreement with the dimensional crossover model; the published agreement with the crossover model, using the four-range simulations, is evidently spurious. In light of this disagreement, it is important to consider whether the all the published Wang-Landau simulation results are flawed. We do not believe this to be
Figure 2.16. The dimensionless specific heat $C_V(T)/(Nk_B)$ of the low-density limit ($N = 1$) and the dimensional crossover model. The low density results compared are Wang-Landau simulations calculated using four overlapping energy subranges (published in [60]), corrected Wang-Landau simulations using three energy ranges, and Metropolis simulations.

The case, due to the smooth behavior of the Wang-Landau simulations for other densities, as well as their agreement with Metropolis simulation.

For the $N = 1$ case, the erratic behavior due to poor overlap between high energy ranges is evident by inspection (Fig. 2.15). But no erratic behavior is visible in the corresponding curves at higher densities ($N = 9, 27, 54$) (Fig. 2.3); the curves joined smoothly across all neighboring ranges. Thus, it is reasonable to believe that those simulations remain accurate. However, their results should be checked by re-simulating the higher densities using three energy subranges instead of four.

The published heat capacities generated by Wang-Landau simulation appeared to agree with independent Metropolis simulation results, even for the improperly simulated $N = 1$ case (Fig. 2.5). It is then potentially questionable whether the corrected Wang-Landau $N = 1$ results can also agree with the Metropolis simula-
however, the main discrepancy between the published and corrected Wang-Landau heat capacities are at intermediate temperatures \( T \sim 175 \text{ K} \), whereas the two curves are in closer agreement at the lower temperatures \( T < 150 \text{ K} \) at which the Metropolis runs were performed. In fact, upon closer inspection, the Metropolis runs show closer agreement to the new three-range Wang-Landau results than to the original published four-range results (Fig. 2.16); the Metropolis runs at the highest temperatures predicted larger heat capacities than did the four-run Wang-Landau simulations.

Therefore, we conclude that the published Wang-Landau results are correct, with the exception of the \( N = 1 \) heat capacity curve corrected in Fig. 2.16, which shows the heat capacity peak to be larger than was published. The new discrepancy between the correct heat capacity and the dimensional crossover model prediction then suggests that the dimensional crossover model is not as accurate as was originally believed, implying that failing to capture the anharmonic behavior of the external potential is not quantitatively prudent.

### 2.5.7.2 Volume density of states

In Sec. 2.5.4.2, the particle energy distributions were explained by appeal to a quantity termed the volume density of states \( f(U) \), which is the volume of space occupied by particles with external potential energies infinitesimally near \( U \). This is proportional to the configurational density of states \( g(U) \) calculated by Wang-Landau simulation, because the number of states within a region of a configuration space is proportional to its volume—assuming that there are no interparticle interactions (low density limit) so that the particle energy is due only to the external (adsorbate-substrate) potential.\(^{15}\)

Since the probability of finding a particle with energy \( U \) is given by \( P(U) \propto g(U) \exp(-\beta U) \), in this article the volume density of states \( f(U) \propto g(U) \) was found by estimating \( P(U) \) by histogramming particle energies from Metropolis simulations and dividing by the Boltzmann factor \( \exp(-\beta U) \).

However, dividing by an exponential factor can be numerically unstable, amplifying sampling errors in the energy histograms. It is better to use the Wang-Landau estimate of the density of states directly. Alternatively, the volume density of states can be calculated directly by dividing (configuration) space into a 3D grid of small cubical volumes, and histogramming how many cubes have a particular energy—the “volume grid histogram” approach.

Both of these alternatives are compared with the original Boltzmann-weighted estimate of the volume density of states in Fig. 2.15. As can be seen, the density of states estimated by Wang-Landau simulation at low densities agrees quite well

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\(^{15}\)The true density of states counts the states within a volume of phase space, not configuration space, but since the heat capacity can be calculated purely from the configurational density of states, the (phase space) density of states was not simulated.
with the volume density of states calculated directly by the volume grid histogram method. The only discrepancy is that the latter’s peak near the monolayer energy \( U \approx -800 \text{ K} \) is smaller and more rounded than the larger, sharper peak from Wang-Landau simulation. We suggest that this is due to the finite spatial resolution of the cubical grid “softening” the true peak, which could be tested by finite-size scaling analysis of varying grid resolutions.

By contrast, the original volume density of states estimated in this article by weighting the energy probability distribution by the Boltzmann factor is in direct quantitative disagreement with these other two methods, although it shares some qualitative features. We conclude that the Boltzmann weighting method of estimating the volume density of states is unreliable. The conclusions of this article remain unchanged since only qualitative features of the volume density of states were used in our arguments. However, the volume density of states has not yet been quantitatively checked by numerical fitting to determine whether it obeys the predicted asymptotic behavior (e.g., \( f(U) \propto (-U)^{-4/3} \) as \( U \to 0 \)).
3.1 Introduction

Chapter 2 discussed one way in which surface adsorption can give rise to a transition from quasi-one dimensional to two dimensional physics: an increase in adsorbate coverage on a nanotube bundle leads initially to the filling of a 1D groove region between neighboring nanotubes, and eventually to the formation of a 2D film covering the bundle surface.

Another way in which a 1D→2D transition can take place is adsorption within a nanotube, or nanopore. If the pore is small, the adsorbate will be forced to line up on the pore axis in a 1D configuration: the “axial” phase. However, if the pore size is large, it will be energetically favorable for the adsorbate to bind near the inner surface of the pore, forming a 2D film: the “off-axis”, or “(cylindrical) shell” phase. At very low temperatures, even this film can behave quasi-one dimensionally, when there is not enough thermal energy to appreciably excite any azimuthal (rotational) modes. The film becomes more three dimensional in character at higher temperatures when the higher-energy radial modes can be excited and gas can fill the volume of the pore, or when the coverage increases to form a 3D bulk solid, pore size permitting.

The distance from the pore wall at which the adsorbate binds is determined by the equilibrium separation between the adsorbate and substrate, and will be on the order of $\sigma$ for an interaction of the Lennard-Jones type. This corresponds to a location of the adsorbate-substrate potential minimum of $r_{\text{min}} \sim R - \sigma$ as measured from the pore axis. The transition from 2D to 1D physics will occur when the potential minimum is “squeezed” onto the pore axis as the pore size is decreased, or $r_{\text{min}} = 0$, corresponding to a critical pore radius $R_{\text{crit}} \sim \sigma$. These adsorption phases are depicted in Figure 3.1.
For concreteness, we chose to study pores in magnesium oxide (MgO) glass. MgO nanopores can be fabricated as small as 3–8 nm in diameter [51, 52] (see also Sec. 1.3). The adsorbate was chosen to be H_2, which, after ^4\text{He}, is the “textbook” quantum gas, due to its very small mass (see App. A.1).\(^1\) The H_2-MgO potential was taken to be of the Lennard-Jones 12-6 form integrated over the bulk MgO solid; the interaction parameters are given by \(\sigma = 2.014\ \text{Å}, \epsilon = 45.91\ \text{K}\) [5]. The H_2-H_2 interaction potential was taken to be of the Silvera-Goldman form [125]. The H_2 molecule is treated as a spherically symmetric point particle, neglecting internal degrees of freedom.\(^2\)

Below, Section 3.2 is concerned with the structure of the adsorbed H_2, particularly with locating the critical pore radius \(R_{\text{crit}}\) above which the H_2 transitions to a 2D shell film from a 1D confined axial phase. This structural transition is studied path integral Monte Carlo simulation, as well as by classical and semiclassical approximations. The results indicate that quantum H_2 remains on axis for larger pore radii than would be naïvely predicted from the geometry of the classical potential. In addition, Sec. 3.2.2 examines the evidence for H_2-H_2 pairing, or “dimerization”, in this system.

In Section 3.3, our attention turns to the thermodynamic behavior of the H_2-MgO nanopore system. The study opens with a treatment of the spinodal point,

\(^1\)H is lighter than H_2, but it is not chemically inert, and so is less relevant for physisorption.

\(^2\)Internal degrees of freedom for light molecules have been studied in the literature using path integral Monte Carlo methods combined with finite size scaling methods [126].
marking the instability of the homogeneous fluid phase of H\textsubscript{2} in the pore, but proceeds to focus mainly on the heat capacity of the adsorbed H\textsubscript{2}. While path integral simulations are the most general method for treating thermodynamics in this system, their application to this problem is still in progress. Instead, Sec. 3.3.4 studies the heat capacity in the low density limit, using numerical estimates of the adsorbate-substrate energy spectrum. A clear transition from 1D to 2D thermodynamic behavior is found as the pore radius increases past $R_{\text{crit}}$, and the validity of 1D and quasi-1D approximations to this behavior, derived in Secs. 3.3.2 and 3.3.3, is examined.

3.2 Adsorbate structure

3.2.1 Off-axis spreading

3.2.1.1 Classical noninteracting gas

Ignoring interparticle interactions and quantum effects, the most probable location for H\textsubscript{2} to adsorb is at the minimum of the H\textsubscript{2}-MgO potential. This location, $r_{\text{min}}$, governs the adsorbate structure: under these assumptions, the phase will be axial when $r_{\text{min}} = 0$ and off-axis when $r_{\text{min}} > 0$.

The H\textsubscript{2}-MgO potential is by taking the interaction to be of the Lennard-Jones form, and numerically integrating it over a region of space with a cylindrical void excluded. The planar Lennard-Jones parameters $C_3 = 372$ meV\textperiodcentered\AA\textsuperscript{3} and $D = 48$ meV (App. C.3) were obtained from Vidali et al. [5]. The pore potential is plotted in Figure 3.2 for various pore sizes. It is evident that for small $R$, for instance $R = 2.0$ and $R = 2.25$ \AA, the potential minimum lies at $r_0 = 0$. For larger $R$, the axis $r = 0$ becomes a potential maximum, and the minimum shifts off axis to some $r_{\text{min}} > 0$.

The transition from the axial to shell phase can be seen more directly by plotting the location of the potential minimum $r_{\text{min}}$ as a function of pore radius $R$. Figure 3.3 plots a related quantity, the distance of the potential minimum from the pore wall, $R - r_{\text{min}}$. When the minimum occurs on the axis, this quantity equals $R$, since $r_{\text{min}} = 0$, corresponding to the linear portion of Fig. 3.3. When it is located off the axis, as the pore radius increases, the preferred distance of H\textsubscript{2} from the wall should asymptotically approach the equilibrium separation between H\textsubscript{2} and planar MgO, since a plane is the $R \to \infty$ limit of a cylinder of radius $R$. The planar separation can be derived from the known planar parameters $C_3$ and $D$: $z_{\text{min}} = (\frac{2}{3} C_3/D)^{2/3} = 1.73$ \AA. It is somewhat puzzling that the large-$R$ limit of the wall separation for the cylindrical pore is some 7% greater than this, $R - r_{\text{min}} = 1.86$ \AA. Possibly the discrepancy is due to approximation error in the numerical integration.
Figure 3.2. $\text{H}_2$-MgO pore potentials as a function of radial distance from the pore axis, for pore radii $R = 2.0$–$3.5$ Å. Note that the location of the potential minimum shifts from $r_{\text{min}} = 0$ to $r_{\text{min}} > 0$ between $R = 2.25$ and $R = 2.5$ Å.

3.2.1.2 Quantum interacting gas

The preceding analysis has been for a classical, noninteracting gas. A quantum gas with interacting particles can be simulated via the path integral Monte Carlo (PIMC) method (App. B.4, [127, 128]).\(^3\) The PIMC approach to quantum statistical mechanics exploits the following $M$-fold factorization of the partition function in the position representation,

$$Z = \text{tr} \hat{\rho} = \int dR \langle R|\hat{\rho}|R \rangle$$

$$= \int dR \int dR_1 \, dR_2 \cdots dR_{M-1} \langle R|\hat{\rho}^{1/M}|R_1\rangle \langle R_1|\hat{\rho}^{1/M}|R_2\rangle \cdots \times \langle R_{M-1}|\hat{\rho}^{1/M}|R_M\rangle \langle R_M|\hat{\rho}^{1/M}|R \rangle, \tag{3.1}$$

where $\hat{\rho} = \exp(-\beta \hat{H})$ is the unnormalized density matrix and $(R, R_1, \ldots, R_{M-1}, R)$ are the position coordinates of an $M$-step discretized, closed path in configuration space, beginning and ending at position $R$.\(^4\) In the limit that $M \to \infty$, this

\(^3\)We would like to thank Massimo Boninsegni for providing an implementation of the path integral Monte Carlo method.

\(^4\)In the interests of notational simplicity, this expression ignores the permutation symmetry necessary to describe quantum statistical exchange.
Figure 3.3. Distance \((R - r_{\text{min}})\) of the \(H_2\)-MgO potential minimum from the wall of a pore of radius \(R\). The cusp signifying the transition of the minimum away from the axis occurs near \(R = 2.35\ \text{Å}\); the 1D axial phase is to the left of the cusp, and the 2D shell phase to the right. The wall separation asymptotically approaches 1.86 Å for large pores. The dashed horizontal line is the equilibrium separation of \(H_2\) from a planar MgO surface, equal to 1.73 Å, which should correspond to the \(R \to \infty\) limit.

expression becomes an imaginary time path integral over closed, continuous paths.

Path integral Monte Carlo simulation operates by drawing samples from the probability distribution defined by the integrand of Eq. 3.1; the domain of the distribution consists of closed, discretized particle paths (worldlines), rather than particle positions as in classical Monte Carlo. PIMC is among the most general and powerful of quantum Monte Carlo methods,\(^5\) most of which are limited to zero temperature. PIMC works at finite temperature, makes no uncontrolled approximations (e.g., the trial wavefunction \textit{ansatz} in variational Monte Carlo), etc.: it is essentially “exact”, limited only by statistical error that in principle can be made as small as desired.

The distribution of \(H_2\) molecules calculated by PIMC simulation is given in Figure 3.4 for several pore sizes.\(^6\) The axial→shell transition is more apparent in

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\(^5\)For a brief overview of quantum Monte Carlo (QMC) methods, see the computational physics texts of Thijssen and Pang [129, 130] and the Monte Carlo text by Landau & Binder [131]. For a historical literature review of developments in QMC from a chemistry perspective, see Anderson [132].

\(^6\)The simulations were performed at fixed particle number \(N = 28\); the density was not fixed,
Figure 3.4. \( \text{H}_2 \) spatial density distribution (at \( T = 0.5 \text{ K}, \rho = (2.55 \times 10^{-3}/\text{Å})/R^2 \)), for pore radii \( R = 2.5–4.5 \text{ Å} \). Depicted are several hundred superimposed Monte Carlo samples of particle positions (black dots), along with the inner surface of the pore (red circles). (The circles are distorted into ellipses due to the aspect ratio of the figure.)

Figure 3.5, which plots the \( \text{H}_2 \) radial density distribution, along with the corresponding potential energy curves. (This work is also discussed in Sec. 3.5.3.)

The PIMC simulations indicate that the adsorbate appears to move off axis between \( R = 2.5 \) and \( R = 2.75 \text{ Å} \); by comparison, the classical free gas prediction from the potential minimum is for a slightly smaller pore, \( R \approx 2.35 \text{ Å} \). However, this prediction is misleading: even though the potential minimum moves off axis beyond this pore size, the potential is still very flat near the axis (see, e.g., the \( R = 2.25 \) potential curve in Fig. 3.2), and one would expect a substantial number of particles to still concentrate there. Thus, the radial density distribution of even a classical, noninteracting gas might show apparent axial behavior at, say, \( R = 2.5 \text{ Å} \), as in Fig. 3.5. Such a density distribution could be calculated by the ordinary Metropolis Monte Carlo method (App. B.2), although this has not yet been done in this study.

since the pore volume was varied. The value \( N = 28 \) was chosen to approximate the equilibrium linear density of a 1D system (Sec. 3.3.1).
Figure 3.5. \( \text{H}_2 \) radial probability density distribution (at \( T = 0.5 \text{ K} \), \( \rho = (2.55 \times 10^{-3} / \text{Å})/R^2 \)) and MgO pore potential, for pore radii \( R = 2.5, 2.75, 3.0, \) and 3.25 Å, as functions of dimensionless radius \( r/R \). (Radial densities near \( r = 0 \) are exaggerated due to finite size effects after normalizing the radial distribution by 1/(2\( \pi r \)) to obtain the probability density.)

3.2.1.3 Semiclassical noninteracting gas

Intermediate between the classical noninteracting case (studied using the classical potential) and the quantum interacting case (studied using PIMC simulation), a quantum noninteracting gas can be studied analytically—ignoring the quantum statistics of bosons—by the effective potential method ([133], §3.5; [134]; [135]; [136], §3.21, §5; [137]). In this semiclassical approximation, a quantum statistical system can be treated using classical statistical mechanics, by replacing the classical potential with an “effective potential”—derived using path integrals—which receives corrections due to “quantum smearing” from the particles’ zero point motion.\(^7\)

\(^7\)The effective potential can be used in classical Monte Carlo simulations to perform approximate quantum Monte Carlo simulation [138, 139], but this approach has proven to be very limited compared to path integral Monte Carlo ([127], §VIII-D).
Taking quantum effects into account, the axial-to-shell transition can be located more precisely than with our classical arguments, by determining the pore size at which the minimum of the effective potential moves off axis. The effective potential for $H_2$ in an infinitesimally thin nanotube has been calculated previously [140]. Below, we correct some formulas given in that work and extend it to the case of a nanopore within a solid substrate.

Feynman’s original variational approximation to the effective potential ([133], §3.5) in $D$ dimensions is given by,

$$V_{\text{eff}}(\mathbf{r}) = (2\pi \lambda_e^2)^{-D/2} \int d^D \mathbf{r}' V(\mathbf{r}') \exp \left[ -\frac{1}{2} \frac{|\mathbf{r} - \mathbf{r}'|}{\lambda_e} \right], \quad \lambda_e = \hbar / \sqrt{12mT}. \tag{3.2}$$

The effective potential is thus given by the classical potential convolved with a Gaussian of width on the order of $\lambda_e$, the “semiclassical effective thermal wavelength”. This convolution justifies the interpretation of the effective potential as a “smeared” classical potential.

This approximation has been superseded by the Feynman-Kleinert approximation ([134]; [136], §5.3), which uses a quadratic (harmonic oscillator) trial partition function with an oscillation frequency free parameter to be variationally optimized. (Thus, unlike Eq. 3.2, the Feynman-Kleinert expression for the effective potential will not be independent of the specific form of the classical potential $V(\mathbf{r})$, as the optimized oscillator frequency depends on $V$.) The Feynman-Kleinert approximation has in turn been extended to higher orders in a variational perturbation theory which converges with exponential rapidity ([137]; [136], §5). However, the results here are based on the original simple formula of Feynman, Eq. 3.2.

Before proceeding to the study of the nanopore effective potential, we pause to derive a semiclassical expansion for the effective potential. Because $\lambda_e$ quantifies the magnitude of quantum effects (App. A.1), an expansion of the effective potential in powers of $\lambda_e$ gives the quantum corrections to the classical potential. Because the integration kernel of Eq. 3.2 is a Gaussian peaked at $\mathbf{r} = \mathbf{r}'$, it makes sense to expand the classical potential $V(\mathbf{r}')$ in the integrand about $\mathbf{r}$, which to second order is, in abbreviated notation,\(^8\)

$$V(\mathbf{r}') = V(\mathbf{r}) + (\nabla V) \cdot (\mathbf{r}' - \mathbf{r}) + \frac{1}{2!} (\nabla \nabla V) \cdot (\mathbf{r}' - \mathbf{r})^2 + O((\mathbf{r}' - \mathbf{r})^3). \tag{3.3}$$

Upon substituting this expression into the effective potential (Eq. 3.2) and integrating with respect to $\mathbf{r}'$, the odd terms vanish, giving the semiclassical expansion\(^9\)

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\(^8\) In full notation, for instance, the quadratic term is given by the Hessian matrix evaluated at $\mathbf{r}' = \mathbf{r}$, contracted with $(\mathbf{r}' - \mathbf{r}) \otimes (\mathbf{r}' - \mathbf{r})$.

\(^9\) To distinguish notation from the preceding equation, in the following equation $\nabla^2$ is the Laplacian, not the Hessian, and $\langle r \rangle$ means a the function evaluated at $r$, not an abbreviated notation for contraction with a tensor.
\[ V_{\text{eff}}(r) = V(r) + \frac{1}{2} \lambda_e^2 (\nabla^2 V)(r) + O(\lambda_e^4). \]  

(3.4)

We now proceed to consider the specific case of a cylindrically symmetric effective potential, applicable to the study of a nanopore. Converting to cylindrical coordinates, and integrating the angular and longitudinal coordinates out of Eq. 3.2 to determine the effective potential \( V(r) \) in terms of only the radial coordinate, we find the radial effective potential,\(^{10}\)

\[ V_{\text{eff}}(r) = \lambda_e^{-2} \int_0^\infty d\rho V(\rho) \rho I_0\left(\frac{r\rho}{\lambda_e^2}\right) \exp\left[-\frac{1}{2}(r^2 + \rho^2)/\lambda_e^2\right]. \]  

(3.5)

where \( I_0(x) \) is the modified Bessel function (a Bessel \( J \) function of the first kind with imaginary argument),

\[ I_0(x) \equiv J_0(ix) = \sum_{n=0}^\infty \frac{1}{4^n (n!)^2} x^{2n}. \]  

(3.6)

Note that because the integration kernel—the factor in the integrand of Eq. 3.5 multiplying \( V(r) \)—is not a function of \( r - \rho \) (where \( \rho \) is the dummy integration variable), Eq. 3.5 can no longer be interpreted in terms of Gaussian-like smearing. While the Gaussian kernel of Eq. 3.2 is centered near \( r = r' \), the kernel of Eq. 3.5 is centered near \( \rho = r \) only for \( r \gtrsim \lambda_e \), and is centered near \( \rho = \lambda_e \) for \( r \lesssim \lambda_e \). Thus, the effective potential \( V_{\text{eff}}(r) \) for \( r \gtrsim \lambda_e \) is smeared by corresponding points at similar radius in the classical potential \( V(r) \), but the effective potential near the origin \( V_{\text{eff}}(r \approx 0) \) is instead governed by the behavior of the classical potential near \( V(r = \lambda_e) \). These limits are depicted in Figure 3.6.

The radial effective potential also has a semiclassical expansion. Expressing the Laplacian in cylindrical coordinates,

\[ \nabla^2 \equiv \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2}{\partial \theta^2} + \frac{\partial^2}{\partial z^2}, \]  

(3.7)

and discarding the non-radial terms for a cylindrically symmetric potential, Eq. 3.4 gives a semiclassical expansion of the radial effective potential,\(^{11}\)

\[ V_{\text{eff}}(r) = V(r) + \frac{1}{2} \lambda_e^2 [V''(r) + V'(r)/r] + O(\lambda_e^4). \]  

(3.8)

Evaluating the integral for the radial effective potential (Eq. 3.5) is intractable in general, but special cases can be performed. In the case that the classical potential \( V(r) \) is expressed as a Taylor series about the origin,

\[ V(r) = \sum_{n=0}^{\infty} V_0^{(n)} \frac{r^n}{n!}, \quad V_0^{(n)} \equiv \frac{d^n V}{dx^n} \bigg|_{x=0}, \]  

(3.9)

\(^{10}\)This formula corrects the slightly erroneous Eq. 3 in \([140]\), as Eq. 3.2 corrects their Eq. 2; note also that our \( \lambda_e \) is \( 1/\sqrt{2} \) times their \( l \).

\(^{11}\)This expression corrects Eq. 4 in \([140]\).
Figure 3.6. Contour plot of the integration kernel of the radial effective potential, $\lambda_e^{-2} \rho I_0(r\rho/\lambda_e^2) \exp[-(r^2 + \rho^2)/(2\lambda_e^2)]$, from Eq. 3.5. The value of the kernel determines the amount by which the effective potential at radius $r$ is influenced by the value of the classical potential at radius $\rho$. The kernel is peaked near $\rho = r$ for large $r$ and $\rho = \lambda_e$ for small $r$.

The effective potential can itself be evaluated as a series,

$$V_{eff}(r) = \sum_{n=0}^{\infty} 2^{n/2} \Gamma\left(\frac{n}{2} + 1\right) \frac{V_0^{(n)}}{n!} \lambda_e^n \exp\left(-\frac{r^2}{2\lambda_e^2}\right) \times L_{-(\frac{n}{2}+1)}\left(\frac{r^2}{2\lambda_e^2}\right),$$

(3.10)

where

$$L_\nu(x) \equiv {}_1 F_1(-\nu; 1; x),$$

(3.11)

is the Laguerre polynomial generalized to a negative parameter $\nu$, defined in terms of the Kummer confluent hypergeometric function of the first kind,

$$1 F_1(a; b; x) \equiv 1 + \frac{a}{b} x + \frac{a(a+1)}{b(b+1)} \frac{x^2}{2!} + \cdots .$$

(3.12)
The radial potential $V(r)$ is an even function,\textsuperscript{12} which leads the corresponding Laguerre polynomials to simplify; the first three terms in Eq. 3.10 then become

\[ V_{\text{eff}}(r) \approx V_0 + \frac{1}{2} (r^2 + 2\lambda_e^2) V''_0 + \frac{1}{24} (r^4 + 8r^2\lambda_e^2 + 8\lambda_e^4) V^{(4)}_0, \]  

(3.13)

though it should be noted that this is not a power series in $r$, because further terms include low-order powers of $r$.

This series solution for the radial effective potential can be used to check our previous results for the semiclassical series expansion. Collecting terms of Eq. 3.10 in powers of $\lambda$ gives,

\[ V_{\text{eff}}(r) \approx V(r) + \lambda_e^2 \left[ \frac{1}{3} V^{(2)}_0 r^2 + \frac{1}{40} V^{(6)}_0 r^4 + \frac{1}{1260} V^{(8)}_0 r^6 + \ldots \right] + O(\lambda_e^4), \]  

(3.14)

It can be shown\textsuperscript{13} that the series found in the $\lambda_e^2$ term above, whose coefficients are $n/(2n-1)!$, is the Taylor series expansion of $(V'' + V'/r)/2$, in agreement with the second-order term of Eq. 3.8.

The radial effective potential may be numerically integrated using the H$_2$-MgO pore potentials calculated in Fig. 3.2. The effective potential for several pore sizes is calculated and compared to the corresponding classical potentials in Figure 3.7.

As expected, the effective potential approaches the classical potential as temperature increases (see the discussion preceding Eq. 3.3). The effective potential also tends to raise the overall energy, and the potential minimum is moved closer to the origin (pore axis) than in the classical case. The qualitative behavior of the effective potential can be understood in several respects: the energy is raised due to quantum zero point energy. The pore minimum moves inwards because a repulsive hard wall damps the wavefunctions of quantum particles.\textsuperscript{14} The near-axis behavior of the effective potential is relatively unchanged due to the flatness of the corresponding classical potential.

These results corroborate the expectations of the preceding two sections. In Sec. 3.2.1.1 it was found that classically, the (noninteracting) H$_2$ gas moves off axis as the pore radius is increased to 2.30–2.35 Å. In Sec. 3.2.1.2, PIMC simulations found that true, quantum H$_2$ remains on axis longer, moving off axis between 2.5–2.75 Å at $T = 1$ K. Figure 3.8 plots the location of the effective potential minimum as a function of pore radius for various temperatures. These semiclassical results indicate that the quantum gas moves off axis at the same pore size as the classical gas for higher temperatures ($T = 200$ K). However, as the temperature is lowered

\textsuperscript{12}$V(r)$ is even due to the reflection symmetry of a cylindrically symmetric potential $V(r)$ about any plane of fixed azimuthal angle.

\textsuperscript{13}By repeated differentiation of $V(r)$ and application of l’Hôpital’s rule to evaluate terms of the form $V^{(n)}/r^m$ at $r = 0$.

\textsuperscript{14}By contrast, for an intermolecular binding potential, we would expect the effective potential minimum to move outwards from the classical minimum, since in this case the repulsive “hard wall” is at the origin.
Figure 3.7. \( \text{H}_2\text{-MgO} \) pore radial effective potentials at \( T = 100 \) and \( 200 \) K, compared to the corresponding classical potentials, at pore radii \( R = 2.2, 2.4, \) and \( 2.6 \) Å. Note that the quantum behavior described by the effective potential approaches classical behavior in the high temperature limit.

to \( T = 50 \) K, the axial/shell transition is delayed to \( 2.45-2.50 \) Å. Although the semiclassical approximation is not trustworthy at lower temperatures, it is plausible that reducing the temperature to \( 1 \) K can produce a transition between \( 2.5 \) and \( 2.75 \) Å, in agreement with the PIMC simulation results.

### 3.2.2 Dimer structure

Other than the transition from axial to shell adsorption phases, additional structure is visible in the Monte Carlo simulations. The binding of pairs of \( \text{H}_2 \) molecules into dimers at \( T = 1 \) K is visible in Figures 3.9 and 3.10.\(^{15}\) (Here, the term “monomer” is used to refer to a single \( \text{H}_2 \) molecule, and “dimer” is used to refer to the binding of two \( \text{H}_2 \) molecules by weak, long-range van der Waals forces. This is in contrast to the more common chemistry usage in which a “monomer” is an H atom and a “dimer” is the chemical binding of two H atoms into an \( \text{H}_2 \) molecule.)

\(^{15}\)These simulations exhibit the same translational invariance symmetry breaking found in Fig. 2.2, as discussed in the footnote in Sec. 2.2, wherein the particles are not uniformly distributed along the longitudinal axis. This artifact of the simulation cell size is clearer in Fig. 3.11, which exhibits periodic peaks in the \( \text{H}_2 \) pair correlation function at separations of about \( 16 \) Å.
Figure 3.8. Minimum of the H\textsubscript{2}-MgO pore radial effective potential, \( r_{\text{min}} \), as a function of pore radius \( R \), for various temperatures, compared to the minimum of the classical potential. The axial/shell transition occurs at the radius \( R \) for which \( r_{\text{min}} \) becomes nonzero. This transition point for the quantum gas is the same as the classical transition of \( R = 2.3 \ \text{Å} \) when \( T = 200 \ \text{K} \), and increases to 2.45 Å as the temperature of the quantum gas decreases to \( T = 50 \ \text{K} \). (The resolution of the plot and therefore the precision of the estimated transition point is calculated to within 0.05 Å.)

The left plot in Fig. 3.9 depicts superimposed Monte Carlo samples of particle positions, but it implies more dimers than actually exist, since pairs of molecules from different samples may appear near each other by chance when the samples are superimposed on each other. The right plot uses different symbols for each sample, so it is possible to determine whether nearby particles are from the sample and therefore really are neighbors. For clarity, Fig. 3.10 shows the particles from two individual Monte Carlo samples.

Evidence for dimerization can also be seen in a plot of the pair correlation function, Figure 3.11. This function gives the probability \( p(r) \) that two H\textsubscript{2} molecules are separated by a distance \( r \); it can be estimated from a histogram of interparticle distances drawn from Monte Carlo samples.

The pair correlation function shows a peak near \( r = 4.8 \ \text{Å} \), indicating that there is an enhanced probability for pairs of H\textsubscript{2} molecules to exist at that interparticle separation. By comparison, the classical equilibrium separation of H\textsubscript{2} molecules (modeled by the Silvera-Goldman potential) is about 3.4 Å. We attribute this
Figure 3.9. \( \text{H}_2 \) spatial density distribution (at \( T = 1 \) K, \( \rho = 1.46 \times 10^{-3} / \text{Å}^3 \)), for \( N = 28 \) particles in a pore of radius 7 Å. Left: 12 superimposed Monte Carlo samples of particle positions (red crosses). Right: The same, with different symbols used for each sample (12 symbols with 28 points per symbol type).

By inspection of the individual Monte Carlo samples in Fig. 3.10, roughly half of the \( N = 28 \) molecules are bound into dimers. It is possible to analytically estimate the dimer/monomer ratio in this system, by analogy to the calculation of the equilibrium mole fraction in physical chemistry; it is a special case of the Gibbs-Duhem equation for phase equilibrium at constant \( T, P \), and is also analogous to the Saha ionization equation in astrophysics [141]. In equilibrium, the monomer\( \rightarrow \)dimer and dimer\( \rightarrow \)monomer processes will be in detailed balance, and there will be no net change in the free energy, \( F \). Therefore,

\[
\frac{dF}{dN} = \left( \frac{\partial F}{\partial N} \right)_2 - 2 \left( \frac{\partial F}{\partial N} \right)_1 = 0, \tag{3.15}
\]

indicating that the gain in free energy by forming a dimer (2) is balanced by the loss in free energy of two monomers (1). Given the definition of the chemical
Figure 3.10. $\text{H}_2$ spatial density distribution (at $T = 1 \text{ K}, \rho = 1.46 \times 10^{-3}/\text{Å}^3$), for $N = 28$ particles in a pore of radius 7 Å. Depicted are two individual Monte Carlo samples of particle positions extracted from the data in Figure 3.9. Note the presence of dimers ($\text{H}_2$-$\text{H}_2$ pairs) in both plots, as well as possible trimers.

Figure 3.11. $\text{H}_2$ pair correlation function (at $T = 1 \text{ K}, \rho = 1.46 \times 10^{-3}/\text{Å}^3$), for $N = 28$ particles in a pore of radius 7 Å. Inset: An enlarged view of the pair correlation function, near the $r = 4.8$ Å peak that indicates the presence of dimerization.

potential, $\mu = \partial F/\partial N$, this condition reduces to

$$dF = \mu_2 - 2\mu_1 = 0, \quad \mu_2 = 2\mu_1.$$  \hfill (3.16)

The chemical potential of the monomer is just that of an ideal gas while the
chemical potential of the dimer is that of an ideal gas of twice the mass, less the dimer binding energy. If the binding energy per dimer is $\epsilon$, we have in $D$ dimensions,

$$\mu_1 = \frac{1}{\beta} \ln \left( \frac{N_1 \lambda_1^D}{eV} \right),$$

$$\mu_2 = \frac{1}{\beta} \ln \left( \frac{N_2 \lambda_2^D}{eV} \right) - \epsilon,$$

(3.17)

where $\lambda = \sqrt{2\pi\hbar^2/\beta m}$ is the thermal wavelength (App. A.1). Since $\lambda \propto 1/\sqrt{m}$ and $m_2 = 2m_1$, we find $\lambda_2 = \lambda_1/\sqrt{2}$; we will define $\lambda \equiv \lambda_1$ in subsequent discussion.

Substituting these chemical potentials into Eq. 3.16 gives a relation between $N_1$ and $N_2$,

$$\frac{N_2}{N_1^2} = 2^{D/2} \left( \frac{\lambda^D}{V} \right) e^{\beta \epsilon}, \quad N_1 + 2N_2 = N.$$

(3.18)

The dimer-monomer ratio can be solved for,

$$\frac{N_2}{N_1} = \frac{1 + 4x - \sqrt{1 + 8x}}{2(\sqrt{1 + 8x} - 1)}, \quad x = 2^{D/2} \left( \frac{n}{n_Q} \right) e^{\beta \epsilon},$$

(3.19)

where $n \equiv N/V$ is the number density and $n_Q \equiv 1/\lambda^D$ is the “quantum concentration”. In the large-$x$ limit, this reduces to

$$\frac{N_2}{N_1} \approx \sqrt{x/2} = 2^{D/2-1} \sqrt{\left( \frac{n}{n_Q} \right) e^{\beta \epsilon}}, \quad \frac{n}{n_Q} \gg e^{-\beta \epsilon}.$$

(3.20)

For $N = 28$ H$_2$ molecules at $T = 1$ K in a 3D volume $V = \pi R^2 L$, where $R = 7$ Å and $L = 125$ Å, and assuming their binding energy is $\epsilon = 3$ K, Eq. 3.19 predicts a dimer-monomer ratio of 8.5. This is an order of magnitude larger than what is observed in the PIMC simulations, where there are roughly equal numbers of molecules participating in dimers as there are unbound molecules: a dimer-monomer ratio of 0.5.

However, since the H$_2$ forms a 2D film on the inner surface of the pore, it may be more accurate to model this system as a 2D system. For a surface ($D = 2$) of area $A = 2\pi RL$, where $R = 5$ Å is the approximate radius of the cylindrical shell of H$_2$ molecules within a pore of radius 7 Å, Eq. 3.19 predicts a dimer-monomer ratio of 4.4. This ratio is in better agreement with the PIMC simulations, but still differs substantially.

The 2D film calculation is also not fully accurate, since it assumes a planar geometry, rather than a cylindrical geometry. It could be improved by starting from the partition function of a gas restricted to a cylindrical surface. These calculations also neglect the internal rotational-vibrational spectrum of the dimer; these internal degrees of freedom will serve to increase the predicted dimer/monomer
ratio, and thus worsen the agreement with the PIMC results. Finally, we have ignored the possibility of trimers and larger systems of bound particles, although the existence of trimers is suggested in Fig. 3.10. It is unclear how to usefully improve an analytic prediction of the dimer/monomer ratio.

3.3 Adsorbate thermodynamics

3.3.1 Spinodal point

Consider a fluid in a volume whose pressure is being decreased towards zero. A concrete example might be a chamber—such as a nanopore—filled with a liquid, with a piston being withdrawn from the chamber. The fluid will stretch and become rarefied, its density decreasing. At zero pressure, the fluid will be in stable equilibrium, but if the piston is withdrawn further, the fluid will enter a metastable state of tension, or negative pressure: it will tend to suck the piston back into the chamber, resisting its further withdrawal, rather than expelling it in the case of positive pressure.

At a certain negative pressure, the so-called spinodal pressure, the metastable phase becomes unstable. A homogeneous fluid can no longer be supported: as the fluid is pulled apart, the energy barrier against the nucleation of vapor bubbles—i.e., the latent heat of the liquid-gas first order phase transition—vanishes, and the fluid is replaced by an inhomogeneous gas-liquid mixture. This state, the spinodal point, determines the lowest pressure at which the fluid can exist. At the spinodal point, the speed of sound in the fluid drops to zero, as no homogeneous medium exists to support sound waves below this point. The “spinodal line” is the locus of points in the pressure-density plane at which the speed of sound and bubble nucleation energy barrier vanish, separating the metastable and unstable phases of the fluid.

The speed of sound $s$ in a fluid comprised of particles of mass $m$ is given by,

$$s^2 = \frac{\partial P}{\partial (m \rho)},$$

where $\rho$ is the number density of particles in the fluid and $m \rho$ is the corresponding mass density. The spinodal point is therefore located at the minimum of the equation of state, $P(\rho)$, which agrees with its interpretation as the minimum possible pressure in the fluid.

Physically, the speed of sound vanishes at the spinodal point because—to first order—density fluctuations in the fluid cannot produce pressure changes. Sound waves can be supported above the spinodal point because pressure increases with

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This introductory discussion was inspired by the review of liquid helium at negative pressures by Maris and Balibar [142].
density there, so that, for instance, an increase in density creates an increase in pressure which drives the system back toward the equilibrium density (negative feedback); below the spinodal point, an increase in density decreases the pressure, and density fluctuations drive the system away from equilibrium.

In Monte Carlo simulation, the most easily computable quantity is energy, so we would like to express the above condition in terms of energies. We can write the equation of state in terms of the free energy (per particle) $F/N$ as follows:

\[
P \equiv -\frac{\partial F}{\partial V} = -\frac{\partial (F/N)}{\partial (V/N)} \equiv -\frac{\partial (F/N)}{\partial (1/\rho)} = \rho^2 \frac{\partial}{\partial \rho} \left( \frac{F}{N} \right).
\]

Equilibrium occurs at minimum free energy, so the density $\rho_0$ at which $F/N$ is a minimum is the equilibrium density. From the preceding equation, we see that this occurs at zero pressure.

However, the free energy is not accessible to ordinary PIMC simulation.\(^{17}\) As the free energy $F$ is related to the energy $E$ by $F = E - TS$ where $S$ is the entropy and $T$ the temperature, at low temperatures we approximate $F \approx E$, and use the system energy instead of the free energy in the equation of state.

The energy at various densities can be easily determined by PIMC simulation by running the simulation with a variety of numbers of particles.\(^{18}\) The resulting dependence of energy on density can then be fit to a polynomial which can be analytically differentiated to obtain the equation of state as per Eq. 3.22. This is shown in Figures 3.12 and 3.13 for H\(_2\) in a pore of radius $R = 2$ Å at temperature $T = 1$ K. Further differentiation of the equation of state gives the speed of sound, as in Eq. 3.21, from which the spinodal density and pressure may be determined; see Figure 3.14.

In a MgO pore of radius 2 Å—a quasi-1D small pore—at temperature 1 K, the equilibrium linear density of H\(_2\) is found by PIMC simulation to be $\rho_0 = 0.2216$ Å\(^{-1}\), or 4.51 Å/particle. The spinodal density is $\rho_s = 0.2044$ Å\(^{-1}\), or 4.89 Å/particle; the spinodal linear pressure is $P_s = -0.7488$ K/Å, corresponding to a (3D) pressure of $-0.8227$ MPa or $-8.119$ atm. By comparison, other work using diffusion Monte Carlo of 1D H\(_2\) at zero temperature [145] has found a spinodal density of 0.210 Å\(^{-1}\), and quasi-1D H\(_2\) confined in a carbon nanotube of radius 3.42 Å has a spinodal density of 0.209 Å\(^{-1}\).

In spite of the foregoing discussion, the very existence of the spinodal point in this system may be questioned. The spinodal point delineates the boundary between metastable and unstable phases of the system; below it, the system exists in a state of two-phase (liquid-vapor) coexistence rather than as a homogeneous

\(^{17}\)The free energy can be calculated by alternative methods like Wang-Landau Monte Carlo (App. B.3), which have been extended to PIMC simulation [143], but the present work does not make use of those methods.

\(^{18}\)For similar PIMC studies involving 1D \(^4\)He, see Sec. 3.5.2. A PIMC study of 3D \(^4\)He is found in [144].
Figure 3.12. Energy per particle $E/N$ as a function of linear density $\rho$, for $\text{H}_2$ in an MgO pore of radius 2 Å, at $T = 1$ K. Circles are PIMC simulation results, smooth curve is a quartic fit to the PIMC data of the form $E/N = \epsilon_0 + A\rho^2 + B\rho^3 + C\rho^4$, where $\rho_* \equiv (\rho - \rho_0)/\rho_0$, $\rho_0$ is the equilibrium density at which the pressure vanishes (best fit $\rho_0 = 0.2216$ Å$^{-1}$), and $\epsilon_0 = -610.912$ K, $A = 55.782$ K, $B = 335.928$ K, and $C = 740.18$ K are best fit parameters. Inset: An enlarged view of the $E/N$ PIMC data and quartic fit, in the vicinity of the minimum energy. The dotted vertical line is the location of the fit minimum, the equilibrium density $\rho_0 = 0.2216$ Å$^{-1}$. The dashed vertical line is the location of the spinodal point, $\rho_* = 0.2044$ Å$^{-1}$.

fluid. However, compelling theorems forbid the existence of many kinds of phase transitions in 1D (see Sec. 1.1.3) at finite temperature, such as two-phase coexistence. In the quasi-1D geometry of a small nanopore, one might then expect a spinodal transition to be impossible.\(^{19}\) It is possible that the apparent existence of metastable and unstable phases in this system at finite temperature may be a computational artifact, arising from, for instance, approximating the free energy $F$ by the energy $E$—a substitution which is only strictly valid at zero temperature.

Energy vs. density curves, such as in Fig. 3.12, have uses other than for determining the spinodal point; they can also be used to study the applicability of the Landau model of phonon excitations in this system. Treating excitations above

\(^{19}\)Note that the 1D $\text{H}_2$ study of [145] was at zero temperature, so different arguments are needed in that case, but Footnote 14 of [146] indicates that long-range order is impossible in 1D even at zero temperature; short-range order, however, is possible.
Figure 3.13. Equation of state $P(\rho)$ for H$_2$ in an MgO pore of radius $R = 2$ Å at $T = 1$ K; $\rho$ is linear (number) density, determined by a fit to PIMC simulation results. Given are both linear pressure (in K/Å) and 3D pressure (in MPa) scales, related to each other by a factor $k_B \times 10^{10} / (\pi R^2) / 10^6 = 1.0967$.

the ground state as phonons of energy $E_k = \hbar \omega_k$, where $\omega_k$ is the phonon angular frequency at wavenumber $k$, the total excitation energy $\Delta E$ of all phonons is given (in one dimension) by

$$\Delta E = \frac{L}{\alpha} \int dk E_k \langle n_k \rangle,$$

(3.23)

where

$$\langle n_k \rangle = \frac{1}{e^{\beta E_k} - 1}$$

(3.24)

is the mean phonon occupation number at wavevector $k$.$^{20}$

$^{20}$One might wonder why the $z^{-1}$ factor found in the Bose-Einstein distribution (see Eq. 3.29) is absent in the denominator of the $\langle n_k \rangle$ equation, since phonons are scalar quasiparticles and therefore bosons. The answer is that the Bose-Einstein distribution is derived in the grand canonical ensemble, under the assumption that the (average) particle number is fixed; this gives rise to the concept of the chemical potential $\mu$ (and fugacity $z = e^{\beta \mu}$). However, a system of phonon excitations does not have fixed particle number, since arbitrarily many phonons may be excited. In such a system, it is no longer true that $\partial F/\partial N = \mu$; the system is able to minimize its free energy without constraint, giving $\partial F/\partial N = 0$—or effectively $\mu = 0$, $z = 1$—explaining the absence of the $z^{-1}$ factor. See also the discussion in Pathria [118], §7.3, 7.4.
Figure 3.14. Speed of sound $s$ as a function of pressure $P$ for $\text{H}_2$ in an MgO pore of radius $R = 2$ Å at $T = 1$ K; $\rho$ is linear (number) density, determined by a fit to PIMC simulation results. Given are both linear pressure (in K/Å) and 3D pressure (in MPa) scales, related to each other by a factor $k_B \times 10^{10}/(\pi R^2)/10^6 = 1.0967$. The speed of sound vanishes at the spinodal pressure $P_s = -0.7488$ K/Å $= -0.8227$ MPa $= -8.119$ atm.

These equations give

$$\Delta E = \frac{L}{\pi} \int dk \frac{E_k}{e^{\beta E_k} - 1}.$$ \hspace{1cm} (3.25)

In the long-wavelength (low energy) limit, phonons have a linear dispersion $\omega/k = s$, where $s$ is the speed of sound. Substituting $E_k = \hbar sk$ and integrating the preceding equation gives

$$\Delta E = \frac{\pi}{6\hbar s \beta^2} \propto T^2,$$ \hspace{1cm} (3.26)

so the excitation energy increases quadratically with temperature. (This equation is the same as the underived Eqs. 3.50 and 3.51 found later in this chapter.)

The correspondence between the $\Delta E \sim T^2$ behavior predicted by the Landau phonon model and the results of PIMC simulations was not studied here for the H$_2$-MgO pore system. However, such a study of 1D $^4\text{He}$, in collaboration with M. Boninsegni, is discussed in Sec. 3.5.2, outlining the limitations of the phonon model.
3.3.2 1D Bose gas

For very small pores, the adsorbate is confined on-axis along an essentially 1D line. In the low density limit where the gas-gas interactions are insignificant, we may approximate H$_2$ adsorbed in a small pore as an ideal 1D gas obeying Bose-Einstein statistics.

The validity of this approximation deserves further scrutiny. The concept of a noninteracting gas as the low density limit of an interacting gas is more subtle in quantum mechanics than in classical mechanics. In a quantum system, the degree to which particles interact is controlled by two parameters: the length scale of the interparticle interaction potential (such as the Lennard-Jones $\sigma$ parameter), and the thermal wavelength $\lambda$ (App. A.1), which is the length scale over which the quantum mechanics of indistinguishable particles becomes important. Only when the average interparticle spacing is much larger than both parameters can the system be said to be noninteracting.

At the temperatures studied in this work ($T \sim 1$ K), the thermal wavelength ($\sim 1.5$ Å) is smaller than the H$_2$-H$_2$ equilibrium separation ($\sim 5$ Å, estimated in Fig. 3.11). Thus, the noninteracting limit is controlled by the range of the interaction potential, so strictly speaking, the system at low densities may be better approximated by an interacting gas obeying Maxwell-Boltzmann statistics than by a noninteracting gas obeying Bose-Einstein statistics. However, the Bose-Einstein case was studied here in full generality, because the Maxwell-Boltzmann case reduces to it; because it is easier to study analytically than an interacting gas; and because the quasi-1D approximation of the next section has never been studied for Bose-Einstein statistics.

We begin with the density of states for a 1D gas,

$$g(E) = \frac{A}{\sqrt{E}}, \quad A = \frac{L}{\lambda} \sqrt{\frac{\beta}{\pi}},$$

(3.27)

where $\lambda = h / \sqrt{2\pi m T}$ is the thermal wavelength. This may be seen by noting that the number of states within a region of phase space is proportional to the volume of phase space, or (for a single particle),$^{21}$

$$\text{number of states} = \frac{1}{\hbar} \int_0^L dx \int_{-\infty}^{+\infty} dp,$$

(3.28)

where $L$ is the size of the 1D “box” within which the system is confined. Integrating out the position coordinate, the number of states within a small region of momentum space is given by $g(p) dp = L / \hbar dp$, where $g(p)$ is the density of states in momentum space. Changing coordinates from momentum $p$ to energy $E$ and

$^{21}$This is the 1D analogue to the more familiar 3D form, $1/\hbar^3 \int_0^L d^3 x \int_{-\infty}^{+\infty} d^3 p$. Note that there is a factor of $1/N!$ for an $N$ particle system.
equating the number of states in both representations, \( g(p) \, dp = g(E) \, dE \), yields Eq. 3.27.\(^{22}\)

The statistical mechanics of a boson gas in the grand canonical ensemble is dictated by the (unnormalized) Bose-Einstein distribution,

\[
p_{BE}(E) = \frac{1}{z^{-1}e^{\beta E} - 1}; \tag{3.29}
\]

where \( z = \exp(\beta \mu) \) is the fugacity. The average particle number and system energy are given by expectations of the Bose-Einstein distribution weighted by the density of states,\(^{23}\)

\[
N(\beta, \mu) = \int dE \, g(E) \, p_{BE}(E), \tag{3.30}
\]

\[
E(\beta, \mu) = \int dE \, g(E) \, E \, p_{BE}(E). \tag{3.31}
\]

Inserting Eq. 3.27, the above integrals evaluate to

\[
N \lambda / L = \text{Li}_{1/2}(z), \tag{3.32}
\]

\[
E = \frac{1}{2 \beta} \frac{L}{\lambda} \text{Li}_{3/2}(z), \tag{3.33}
\]

\[
E / N = \frac{1}{2 \beta} \frac{\text{Li}_{3/2}(z)}{\text{Li}_{1/2}(z)}, \tag{3.34}
\]

where \( L \) is the system length and \( \text{Li}_\nu(z) \) is the polylogarithm function.\(^{24}\)

The heat capacity is \( C_V = (\partial E / \partial T)_{N,V} \), with the derivative taken at fixed particle number as well as volume. The specific heat is \( c_V = C_V / N = [\partial (E / N) / \partial T]_{N,V} \); the division by \( N \) can be taken inside the derivative, even though \( N \) is a function of \( T \), because the derivative is taken at fixed \( N \). The specific heat can be expressed as

\[
c_V = \frac{\partial}{\partial T} \left[ \frac{T}{2} \frac{\text{Li}_{3/2}(z)}{\text{Li}_{1/2}(z)} \right]. \tag{3.35}
\]

We can write

\[
c_V = \frac{\partial(T f/2)}{\partial T} = \frac{1}{2} \left( f + T f' \frac{d}{dT} \right), \quad f(z) = \frac{\text{Li}_{3/2}(z)}{\text{Li}_{1/2}(z)}. \tag{3.36}
\]

\(^{22}\)A factor of 2 is acquired upon changing the lower limit of integration from \(-\infty\) for the vector \( p \) to 0 for the scalar \( E \).

\(^{23}\)It is unnecessary to pull the ground state out of the \( N \) integral as a separate term as in the 3D case, because the 3D density of states (\( \propto \sqrt{E} \)) gives zero weight to the ground state \( E = 0 \) in the integral; this is not the case in 1D. This is intimately related to the absence of homogeneous Bose-Einstein condensation in \( D < 3 \) (see Sec. 1.1.3).

\(^{24}\)Note that \( N \lambda / L = \sqrt{n / n_Q} \) where \( n \) is the linear density and \( n_Q \) is the one dimensional quantum concentration (App. A.1).
Figure 3.15. Specific heat of an ideal one dimensional Bose gas as a function of temperature, for H$_2$ at density $N/L = 0.224$ Å$^{-1}$.

Exploiting a polylogarithm identity, $Li'_\nu(z) = Li_{\nu-1}(z)/z$, we obtain

$$f' = \frac{1}{z} \left[ 1 - \frac{Li_{3/2}(z) Li_{-1/2}(z)}{Li_{1/2}(z)} \right]. \quad (3.37)$$

To determine $dz/dT$, we return to Eq. 3.32. Differentiating with respect to temperature, we have $d(N\lambda/L)/dT = Li'_{1/2}(z)(dz/dT)$; applying the derivative identity, the right hand side becomes $z^{-1} Li_{-1/2}(z)(dz/dT)$, and using $\lambda = \sqrt{\hbar^2/(2\pi mT)}$, we find $d\lambda/dT = -\lambda/(2T)$. Therefore,

$$\frac{dz}{dT} = \frac{z}{2T} \frac{Li_{1/2}(z)}{Li_{-1/2}(z)}. \quad (3.38)$$

Inserting Eqs. 3.37 and 3.38 into Eq. 3.36, we finally obtain for the specific heat,

$$c_V = \frac{C_V}{N} = \frac{3}{4} \frac{Li_{3/2}(z)}{Li_{1/2}(z)} - \frac{1}{4} \frac{Li_{1/2}(z)}{Li_{-1/2}(z)}. \quad (3.39)$$

The specific heat as a function of temperature is depicted in Figure 3.15. The temperature dependence of the fugacity on temperature, $z(T)$, was obtained by numerical solution of Eq. 3.32 (note that $\lambda$ depends implicitly on $T$).
The low and high temperature limits of the specific heat can be recovered analytically. It can be shown that \( \text{Li}_\nu(0) = 0 \), and \( \text{Li}_\nu(1) = \infty \) for \( \nu \leq 1 \) ([118], App. D). Since \( \lambda \to \infty \) as \( T \to 0 \) and \( \lambda \to 0 \) as \( T \to \infty \), the low and high temperature limits are achieved when \( z = 1 \) and \( z = 0 \), respectively (see Eq. 3.32).

From the series expansion,

\[
\text{Li}_\nu(z) = \sum_{l=1}^{\infty} \frac{z^l}{l^\nu},
\]

we see that \( \text{Li}_\nu(1) \) diverges less quickly (or even converges, for \( \nu > 1 \)) than \( \text{Li}_{\nu-1}(1) \), and that \( \text{Li}_\nu(0) \) and \( \text{Li}_{\nu-1}(0) \) converge or diverge at the same rate. We can then evaluate the low and high temperature limits of Eq. 3.39:

\[
c_V = 0, \quad T \to 0 \ (z \to 1),
\]

\[
c_V = \frac{1}{2}, \quad T \to \infty \ (z \to 0).
\]

The vanishing specific heat at low temperature is expected for any physical system on the basis of the third law of thermodynamics (Nernst’s theorem), which states that the entropy of a system vanishes at absolute zero. The first law of thermodynamics (at fixed \( N, V \)) in differential form states that \( dE = T \, dS \) where \( S \) is the entropy. Integrating the first law, \( S = \int dE/T = \int (dE/dT)(dT/T) \), or \( S = \int dT \, C_V(T)/T \). The heat capacity must vanish at \( T = 0 \) for this integral to itself vanish.

The high temperature limit of \( \frac{1}{2} \) for the specific heat is also expected, since the classical limit is approached at high temperatures (App. A.1), and \( \frac{1}{2} \) is the specific heat dictated by the equipartition theorem for a one dimensional ideal classical gas.

### 3.3.3 Quasi-1D Bose gas

A gas in a cylindrical pore is free in the longitudinal (axial) direction and confined in the transverse directions. The energy spectrum will correspondingly have a continuum of longitudinal states, but the transverse states will be quantized. If the temperature \( T \) is low compared to the energy gap \( \epsilon \) between the ground and first excited (transverse) state \( (T \ll \epsilon) \), then the transverse states will be difficult to excite, and the system is approximated by a 1D gas, as in Sec. 3.3.2.

The simplest improvement to the 1D gas approximation is to take the first excited transverse state into account. This is called the “quasi-1D” approximation, and its derivation is similar to the 1D gas. We assume that the ground state is nondegenerate, but allow the excited state to have a degeneracy \( g \):\textsuperscript{25} for a

\textsuperscript{25}The degeneracy \( g \) is an integer counting how many distinct quantum states have transverse energy \( \epsilon \). It is not to be confused with the density of states \( g(E) \), which is a measure of how many states have longitudinal energy \( E \); nor is it to be confused with the concept of exchange degeneracy of indistinguishable particles in quantum statistics.
cylindrical geometry, the lowest transverse states will be azimuthal states, which are doubly degenerate ($g = 2$), corresponding to clockwise or counterclockwise orbital motion. (Radial motion has a higher energy gap than azimuthal motion, so it is ignored in this approximation.)

Assuming the transverse ground state (0) to have zero energy and the excited state (1) to have energy $\epsilon$, the average particle number and system energy are given by,

$$N(\beta, \mu) = N_0 + N_1 = \int dE g(E) p_{BE}(E) + g \int dE g(E) p_{BE}(E + \epsilon), \quad (3.42)$$

$$E(\beta, \mu) = E_0 + E_1 = \int dE g(E) E p_{BE}(E) + g \int dE g(E) (E + \epsilon) p_{BE}(E + \epsilon), \quad (3.43)$$

where $p_{BE}(E)$ is the Bose-Einstein distribution defined in Eq. 3.29 and $g(E)$ is the 1D density of states (Eq. 3.27). Note that $E$, as before, refers to the continuum of longitudinal energies.

Upon integration, these equations become,

$$N\lambda/L = \text{Li}_{1/2}(z) + g\text{Li}_{1/2}(e^{-\beta\epsilon}z), \quad (3.44)$$
$$E = \frac{1}{2\beta} \frac{L}{\lambda} \left[ \text{Li}_{3/2}(z) + g\text{Li}_{3/2}(e^{-\beta\epsilon}z) + 2g\beta\epsilon\text{Li}_{1/2}(e^{-\beta\epsilon}z) \right], \quad (3.45)$$
$$E/N = \frac{1}{2\beta} \frac{\text{Li}_{3/2}(z) + g\text{Li}_{3/2}(e^{-\beta\epsilon}z) + 2g\beta\epsilon\text{Li}_{1/2}(e^{-\beta\epsilon}z)}{\text{Li}_{1/2}(z) + g\text{Li}_{1/2}(e^{-\beta\epsilon}z)}. \quad (3.46)$$

The dependence of temperature on fugacity, $T(z)$, may be obtained from a perturbation expansion of Eq. 3.44 with $e^{-\beta\epsilon}$ as the small parameter (implying the expansion is good at low temperatures, $T \ll \epsilon$). To second order, this expansion is:

$$T(z) \approx T_0 + T_1 + T_2, \quad T_0 = \frac{\hbar^2}{2(2\pi m)} \text{Li}_{1/2}^2(z), \quad T_1 = -\frac{2g\epsilon z e^{-\epsilon/T_0}}{\text{Li}_{1/2}(z)} T_0, \quad T_2 = \left( \frac{3}{4} + \frac{\epsilon}{T_0} \right) \frac{T_0^2}{T_0^2}. \quad (3.47)$$

The temperature derivative of $E/N$ can be analytically performed to obtain the specific heat, but the resulting expression is cumbersome. Instead, the derivative can be numerically approximated by finite differences, and the temperature dependence of fugacity determined by numerical solution of Eq: 3.44 for $z(T)$. The resulting temperature dependence of specific heat for a quasi-1D gas for various energy gaps $\epsilon$ is depicted in Figure 3.16.

Many of the features of Fig. 3.16 can be explained qualitatively. First, unlike the 1D gas, the quasi-1D gas has a peak in the heat capacity. This is an analogue of the Schottky anomaly for a two-state system (App. A.2.2): the heat capacity
Figure 3.16. Specific heat of an ideal quasi-one dimensional Bose gas as a function of temperature, for H$_2$ at density $N/L = 0.224$ Å$^{-1}$, for (from left to right) $\epsilon = 1, 3, 5, 10,$ and $20$ K. The black curve is the 1D Bose gas from Fig. 3.15. The blue curves are for a nondegenerate excited state ($g = 1$); the green curves are for a doubly-degenerate excited state ($g = 2$). A dashed line at $c_V = \frac{1}{2}$ indicates the 1D classical limit.

is enhanced when the thermal energy $T$ approaches the energy gap $\epsilon$. This occurs when the available thermal energy becomes large enough for significant promotion into the excited state to take place. It also explains why the peak is shifted to higher temperatures for higher energy gaps.

Numerical experiments indicate that the location of the peak asymptotically approaches $T/\epsilon = 0.431$ as $\epsilon \to \infty$ for $g = 1$. This can be compared, for instance, to the “2/5 rule” of a classical 2-state system (App. A.2.2), in which the heat capacity peak appears at $T/\epsilon = 0.417 \approx 2/5$. It may be of further interest to understand the origins of this result, considering that the $\epsilon \to \infty$ limit corresponds to a 1D gas which has no energy gap and hence no peak at any location.

The enhancement in heat capacity is larger in magnitude when the excited state is degenerate. This is to be expected, since with more high-energy states available, it is easier to increase the system energy. For the same reason, the peak in the heat capacity occurs at a slightly lower temperature for the degenerate system
than for the corresponding nondegenerate system: at a fixed temperature, it is
more favorable for promotion to occur into the excited state when that state is
degenerate.

The asymptotics of the heat capacity are of interest as well. Note that the
curves in Fig. 3.16 with smaller energy gaps $\epsilon$ are the first to depart from the pure
1D gas heat capacity at low temperatures, but are also the first to approach the 1D
gas at high temperatures. Their early departure from 1D behavior occurs because
a smaller energy gap is easier to excite at low temperatures, so the heat capacity
will more rapidly differ from the 1D case which has no excited transverse state.

A smaller energy gap, however, leads to earlier convergence to the 1D gas
behavior at high temperatures, because when $T \gg \epsilon$, the energy gap disappears
in comparison to the thermal energy. What remains is effectively a 1D gas with
a $(g + 1)$-fold ground state degeneracy: the nondegenerate true ground state with
zero energy, plus $g$ excited states with nearly zero energy. Such a gas has a specific
heat identical to the nondegenerate 1D gas studied in Sec. 3.3.2; the formulas for
$N$ and $E$ pick up an extra $g + 1$ factor due to the degeneracy of each energy state,
but it cancels out for $E/N$ and therefore for the specific heat.

Another point of note is that these specific heat curves have a low temperature
inflection point; they start out convex when they match the convexity of the 1D gas
which they approach as $T \to 0$; they turn concave briefly as they depart from the
1D gas behavior, and become convex again when they approach the heat capacity
peak.

3.3.4 Noninteracting Bose gas in a nanopore

Having derived results for a quasi-one dimensional Bose gas, we can see how well
this approximation corresponds with a gas confined on axis in a small pore. To sim-
plify matters, we neglect interactions between the adsorbate molecules. The equations
for the particle number and system energy for the quasi-1D case (Eqs. 3.42,
3.43) are generalized to sum over the full transverse energy spectrum $\{\epsilon_{n,\nu}\}$:

$$N(\beta, \mu) = \sum N_\epsilon = \sum_{n, \nu=0} g_\nu \int dE \, g(E) \, p_{BE}(E + \epsilon_{n,\nu}), \quad (3.48)$$
$$E(\beta, \mu) = \sum E_\epsilon = \sum_{n, \nu=0} g_\nu \int dE \, g(E) \, (E + \epsilon_{n,\nu}) \, p_{BE}(E + \epsilon_{n,\nu}), \quad (3.49)$$

where the azimuthal degeneracy factor $g_\nu$ equals 1 for $\nu = 0$ (no angular momen-
tum) and 2 for $\nu > 0$ (corresponding to the $\pm \nu$ (counter-)clockwise rotational
states).

The energy spectrum, shown in Figure 3.17, was computed from the pore poten-
tial by numerical solution of the time-independent Schrödinger eigenvalue equation
in cylindrical coordinates, via the Numerov-Cooley algorithm \cite{147, 148}. The energy gap between the ground and first excited state narrows dramatically as the pore radius exceeds $\sim 4 \text{ Å}$; this is roughly when we expect thermodynamic departure from 1D axial behavior. \footnote{We would like to thank Roman Schmied for providing an implementation of the Numerov-Cooley algorithm.}

Similarly to the procedure followed in the quasi-1D case, Eq. \ref{eq:3.48} was solved numerically for the chemical potential $\mu$ in terms of the particle number $N$, and inserted into Eq. \ref{eq:3.49} to find the system energy as a function of particle number, $E(\beta, N)$. From this, the heat capacity was obtained by a finite difference approximation to the temperature derivative, $(\partial E/\partial T)_N$.

The resulting specific heats, for a variety of pore sizes and at two selected temperatures, are displayed in Figure \ref{fig:3.18}. The specific heat starts out less than the classical 1D limit of $\frac{1}{2}$, because the temperatures studied are below the onset of classical behavior (see Fig. \ref{fig:3.15}). However, as the energy gap between the ground and first excited states decreases, the specific heat begins to rise, as found in the quasi-1D case for temperatures comparable to the energy gap (Fig. \ref{fig:3.16}). For large pores, the classical 2D limit of 1 for the specific heat is asymptotically approached.

Figure \ref{fig:3.18} also compares the predictions of the quasi-1D model, in which only the ground and first excited states are considered in the spectrum. As expected, the quasi-1D approximation is good when the energy gap is much larger than the temperature, but breaks down when the energy gap is comparable to the temperature, as the higher excited state energies are close to the thermal energy and can no longer be ignored. \footnote{The energy gaps narrow with increasing $R$ because the spectrum of the Schrödinger equation in a cylindrical geometry is $E = \hbar^2 k_z^2/(2m) + \hbar^2/(2m)\nu^2/R^2$, so the transverse gap decreases like $1/R^2$. The $\hbar^2/(2mR^2)$ factor is analogous to $\hbar^2/(2m)$, with the moment of inertia $mR^2$ playing the role of mass.}

\footnote{In related work, the 1D to 2D transition in a nanotube was studied in the quasi-1D approximation by Stan and Cole \cite{149}. They recovered the 2D limit even in the quasi-1D approximation by averaging over a range of energy gaps $\epsilon$.}

\footnote{It might be mildly interesting to calculate the heat capacity asymptotically approached by the quasi-1D approximation in the large-$R$ limit; the $\epsilon = 5 \text{ K}$ curve in Fig. \ref{fig:3.18} suggests that this value is not the 1D value of $1/2$ one might expect.}

### 3.3.5 Interacting Bose gas in a nanopore

The case of a realistic, interacting $\text{H}_2$ gas is too difficult to be attacked by the preceding semianalytic methods. Path integral Monte Carlo simulations are the tool of choice for an interacting quantum system. However, the fluctuation formula for heat capacity used in classical Monte Carlo (Sec. \ref{sec:2.3.1}, App. \ref{app:A.2.1}) requires adaptation to PIMC, and proves not to be a reliable statistical estimator \cite{150}. Improved heat capacity estimators exist (e.g., \cite{151, 152}), but their implementation is less straightforward.
Figure 3.17. Energy spectrum $E_{n,\nu}$ of H$_2$ in a MgO pore, as a function of pore radius $R$. (The $n, \nu$ are the radial and azimuthal quantum numbers, respectively.) Black curves are the ground and first four excited radial states in the lowest azimuthal state ($E_{0,\nu}, \ldots, 4_0$); these states are nondegenerate ($g = 1$). The lowest lying curve is the ground state, $E_{0,0}$. Colored curves are for the first five excited azimuthal states ($E_{0,0}, \ldots, 4_1, \ldots, 5_5$); these energies are doubly degenerate ($g = 2$). Inset: The same spectrum, plotted with the minimum of the MgO pore potential for each pore size (dashed curve), $V_{\text{min}}(R)$, to indicate the zero point energy $E_{0,0} - V_{\text{min}}$.

Alternatively, the Wang-Landau algorithm could be adapted to the PIMC method [143], and heat capacities calculated from the density of states (as in Sec. 2.3.2), although this would require substantially more modification to an existing PIMC code than the addition of a heat capacity estimator, and its efficacy in calculating heat capacities is unknown.

The heat capacity of course can also be calculated directly from the derivative $\partial E/\partial T$, either by finite differences or—more often in practice—by analytically differentiating a fit function of known form [127], although a number of data points at closely spaced temperatures and some finesse is required to produce accurate estimates. Work on PIMC simulation of H$_2$ heat capacities in an MgO pore is in progress.
Figure 3.18. Above: Specific heat of noninteracting H$_2$ gas in a MgO pore as a function of pore radius $R$, at fixed linear density $N/L = 0.224$ Å$^{-1}$ (3D density $\rho = N/L/(\pi R^2)$), for $T = 1$ and 5 K (solid curves). Contrasted are the predictions of the quasi-1D model with an energy gap $\epsilon \equiv \epsilon_{0,1} - \epsilon_{0,0}$ determined by the ground state and first azimuthal state (dashed curves). (The quantum numbers $n, \nu$ of $\epsilon_{n,\nu}$ denote radial and azimuthal excitations, respectively.) The horizontal dashed lines are the classical 1D and 2D limits of $\frac{1}{2}$ and 1, respectively. Below: The energy gap between the ground state ($\epsilon_{0,0}$) and the first four azimuthal excitations of the ground radial state ($\epsilon_{0,\{1\ldots4\}}$). The horizontal dashed lines correspond to energy gaps of 1 and 5 K.
3.4 Limitations and future work

The studies in Sec. 3.2 found that, as the pore diameter is increased past 0.5–0.55 nm, the H\(_2\) gas moves from being confined on axis into a cylindrical shell monolayer on the inside surface of the pore. However, it is not currently possible to fabricate MgO pores with such a small size; they can realistically be produced with diameters of 3–8 nm [51, 52]. This implies that the axial→shell transition characterized in this work cannot yet be studied experimentally in this system. Axial confinement is experimentally possible to study in other pore-like systems, such as carbon nanotube interiors. It may also be possible to study the axial phase in this system when multilayer adsorption is present, as previously adsorbed layers will serve to reduce the effective pore radius. One such system is discussed in [153].

While the critical pore radius \(R_{\text{crit}}\) at which the axial to shell transition occurs was studied by classical (Sec. 3.2.1.1) and semiclassical (Sec. 3.2.1.3) approximations, the character of the full interacting quantum system can be studied only by path integral Monte Carlo (PIMC) simulations (Sec. 3.2.1.2). It was found that the H\(_2\) remains confined in its axial phase for slightly larger pores in the real quantum system than for a system in which the H\(_2\) molecules are treated classically \((R_{\text{crit}} = 2.5–2.75 \text{ Å} \text{ at } T = 1 \text{ K and } \rho = (2.55 \times 10^{-3}/\text{Å})/R^2)\), compared to a classical low-density prediction of \(R_{\text{crit}} = 2.3–2.35 \text{ Å}\).

In future work, PIMC simulations could be performed at a variety of temperatures to determine the dependence of the critical radius on temperature; we generically predict that the critical radius will increase with decreasing temperature, as high temperatures correspond to classical behavior. The simulations could also be repeated at a finer granularity of pore sizes to more precisely locate the critical pore radius. The axial/off-axis transition was located by visual inspection of the most probable location at which H\(_2\) molecules are to be found (Fig. 3.5); possibly a better characterization of their location would be to plot their mean radius \(\langle r \rangle\) as a function of pore size \(R\).

The semiclassical study of the nanopore effective potential in Sec. 3.2.1.3 could be improved by replacing Feynman’s original approximation to the effective potential (Eq. 3.2) with the more accurate Feynman-Kleinert approximation or higher-order approximations from the variational perturbation theory, potentially allowing the higher-temperature semiclassical results to be extended down to the \(T \sim 1 \text{ K}\) temperature range, so that they may be compared to the results of the low temperature PIMC simulations. Currently, the semiclassical estimates of \(R_{\text{crit}}\) are only suggestively compatible with the PIMC estimates by extrapolation to low temperatures.

The PIMC simulations indicated the presence of “dimer” states, weakly-bound pairs of H\(_2\) molecules, and possibly even “trimers” (trios of molecules). A quantitative method of measuring the number of dimers present in the system needs to be developed in order to make concrete predictions. Back-of-the-envelope ana-
lytic estimates of the dimer/monomer ratio are about an order of magnitude larger than the ratio estimated from visual inspection of PIMC sample configurations. The analytic estimates are crude and need to be improved, although some proposed improvements such as including the dimer’s rotational-vibrational spectrum would only serve to increase the discrepancy between the analytic and simulation predictions.

In Sec. 3.3.1 the spinodal point at which the homogeneous fluid phase destabilizes into an inhomogeneously coexisting gas-fluid phase was determined at $T = 1$ K for a pore radius of $R = 2$ Å. However, the existence of this transition in a quasi-1D system may be questioned on theoretical grounds, concerning the non-existence of many phase transitions in one dimension; more consideration of theory is necessary to resolve this question, or alternatively the results of simulations to which the free energy of the system is accessible. The results found here could also be repeated for different temperatures and pore sizes. The applicability of the Landau phonon model to this system can also be studied from the simulated energy vs. density curves, although the results would only be approximate at nonzero temperature unless a simulation capable of calculating free energies were used.

The heat capacity calculations indicating a 1D to 2D thermodynamic transition with increasing pore radius in Sec. 3.3.4 were calculated from the lowest lying energy levels of the $\text{H}_2$-pore energy spectrum, neglecting interparticle interactions. PIMC simulations are needed to calculate heat capacities in the interacting system; the existing noninteracting results can be compared to PIMC simulations without interactions to check the validity of the simulations before moving to simulations with interactions.

General extensions to this work would be to calculate all of the phenomena studied here at a wider range of temperatures, densities, and pore sizes. In particular, all of the densities studied here were fairly low, to minimize PIMC simulation time. Thus, interparticle interactions and Bose-Einstein quantum statistics have relatively minor influence, other than the dimer structure observed in Sec. 3.2.2 due to $\text{H}_2$ pair bonding. It would be interesting to study what effects the interactions in this many-body system have upon the results found here.
3.5 Article: “Quantum fluids in nanopores”

Below is the text of an article to be published in Proceedings of the 13th International Conference on Recent Progress in Many-Body Theories (QMBT13) [154], ©2006 World Scientific, with minor alterations from the published version.

Quantum fluids in nanopores

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Abstract

We describe calculations of the properties of quantum fluids inside nanotubes of various sizes. Very small radius ($R$) pores confine the gases to a line, so that a one-dimensional (1D) approximation is applicable; the low temperature behavior of 1D $^4$He is discussed. Somewhat larger pores permit the particles to move off axis, resulting eventually in a transition to a cylindrical shell phase—a thin film near the tube wall; we explored this behavior for $H_2$. At even larger $R \sim 1$ nm, both the shell phase and an axial phase are present. Results showing strong binding of cylindrical liquids $^4$He and $^3$He are discussed.

3.5.1 Introduction

The discovery of carbon nanotubes has provided a playground for theoretical physics analogous to that (~1970) based on the discovery of adsorption on flat, well-characterized surfaces. In the former case, excitement arises from the tantalizing possibility that one-dimensional (1D) physics can be tested by studying adsorbed gases near nanotubes, just as studies of monolayer films provided tests of 2D physics.

Many groups have explored the properties of quantum fluids on the external surface of nanotube bundles and the interstitial regions within the bundles, stimulated by both the intriguing geometry and several experimental results [85, 155, 92, 156, 157, 108, 20, 158, 146, 159, 160, 161, 145, 162]. Our group has predicted several novel phase transitions for interstitial quantum fluids, including a high temperature (liquid-vapor) condensation and a BEC that exhibits 4D (!) thermodynamic properties [157, 108, 20]. This paper summarizes instead diverse results concerning quantum fluids inside single nanotubes, obtained with a variety of methods. These studies are far from complete, with significant theoretical questions yet to be answered. The following section discusses the case of $^4$He in 1D, with applications to small radius ($R$) pores. Section 3.5.3 explores the behavior of absorbed $H_2$ as $R$ increases, so that the 1D approximation breaks down. Section 3.5.4 discusses the nature of films in large pores ($R \sim 1$ nm), where one encounters both a “cylindrical
shell” phase of the film on the surface and a so-called “axial” phase, which is very much like the 1D system in the small $R$ case.

Throughout this paper we omit the details of both the adsorption potential and the techniques used in the calculations. Those can be found in existing publications, as well as a thesis and longer article currently being drafted [158]. Our emphases are new results, qualitative behavior, and significant open questions.

### 3.5.2 Behavior in the 1D limit

The 1D $^4$He system is interesting for several reasons. One is that the liquid is barely bound (by about 1.7 mK) and very rarefied (mean spacing about 2.7 nm!); in fact, the venerable Lennard-Jones (LJ) pair potential is too weakly attractive to produce this bound state [146, 159, 160, 161]. A related fact is that the threshold interaction strength for 1D binding of the liquid state coincides with that of the 1D dimer [160, 161]. Recently, L.W. Bruch and C. Carraro (private communications) have shown that the cohesive energy of the 1D many-body system has the 1D dimer binding energy as a lower limit, the two energies possibly coinciding. There is a closely related, intriguing aspect to the dimer problem. Consider the three-dimensional (3D) dimer problem, focusing on the $s$-wave channel. The radial Schrödinger equation for that problem coincides with the Schrödinger equation for the 1D dimer. A key difference between $D = 1$ and $D = 3$ is the requirement that the wave function $\psi(r)$ vanish at 3D separation $r = 0$. However, this difference is inconsequential for a 1D system involving hard-core interactions. Hence, the 3D wavefunctions and spectra coincide, at least for the $s$-channel, with those of the 1D problem. Putting all of this information together, it might be “expected” theoretically that all of the three energies agree, with the common value 1.7 mK.

Recently, we have studied the thermal properties of 1D liquid $^4$He, using the path integral method [127, 128]. If one were to anticipate the behavior theoretically, one might treat the system with the Landau model, based on elementary excitations above the ground state. In the limit that the low-lying excitations are phonons, with $T = 0$ speed $s(\rho)$ at density $\rho$, this model predicts that the energy per particle $\Delta E$ (relative to the ground state energy) satisfies

$$\Delta E(T) = F(k_B T)^2,$$

(3.50)

$$F = \frac{\pi/6}{\hbar s \rho}.$$  

(3.51)

Preliminary results of the path integral calculations, in Fig. 3.19, are consistent with this prediction at low $T$ and high $\rho$; e.g., values of the coefficient $F$ in Eq. 3.50 fit to the data at $\rho = 2.5/\text{nm}$ (and higher) agree with the value predicted by Eq. 3.51. At $\rho = 2/\text{nm}$ and below, instead, the values of $F$ begin to disagree and the departure from the quadratic dependence occurs at lower $T$. The latter is not surprising because the $T^2$ dependence of $\Delta E$ is expected only far below the 1D
Debye temperature, $\Theta = \hbar \rho / (k_B \pi)$. Since $\Theta \sim 8$ K at $\rho = 2$ nm and $\Theta \sim 30$ K at $\rho = 2.5$ nm, different behavior of $\Delta E$ is expected for the two densities at 5 K.

Departure from simple model behavior at very low $\rho$ is also expected on general grounds, since the speed of sound becomes imaginary below the spinodal density, $\rho \sim 0.245$ nm (compared to an equilibrium density 0.36 nm). The phonon theory has no meaning at such low $\rho$. The observed departure from Landau-like predictions occurs at much higher density than that, however. This empirical behavior remains to be understood. At very low density, one might be inclined to use a virial expansion. Šiber has evaluated the first virial correction to the 1D $^4$He system. His results show significant departure from the classical specific heat ($1/2$ Boltzmann per atom) at relatively high $T$, even for very low density. This has nothing to do with exchange, which does not contribute because of the hard core repulsion [163, 164]. One expects higher order virial terms to contribute in addition, making this system particularly interesting to explore experimentally.

### 3.5.3 Spreading away from the axis

The $T = 0$ properties of 1D H$_2$ were first calculated by Boronat, Gordillo, and Casulleras [145]. Here, we report preliminary results of finite $T$ behavior as the radius is increased from a very small value to $R = 0.7$ nm.
Assuming a Lennard-Jones interaction between the gas adsorbate molecules and the inner pore surface, as adsorbate density is increased the gas will begin to adsorb onto the pore as a cylindrical shell film, at a distance from the surface on the order of the LJ parameter $\sigma$. However, we expect that if the radius $R$ of the pore is less than this characteristic distance, the gas-surface repulsion will heavily restrict the transverse motion of the gas, and the two-dimensional (2D) shell will collapse into a 1D line of molecules on the pore axis.

Geometrically, this axial compression at small pore radii exhibits itself in the nanopore potential as a transition from a minimum near $r \sim R - \sigma$ and a maximum at $r = 0$ (i.e., an off-axis potential well) when $R \gtrsim \sigma$, to a simple minimum at $r = 0$ when $R \lesssim \sigma$ (an on-axis potential well). For the case of an infinitesimally thin tube, this transition is analytically known to occur at $R \approx 1.212\sigma$ [149]. We do not know an analogous analytic result for the case studied here, a pore within bulk material, but numerically the transition point is similar.

For concreteness, we chose to study pores in MgO glass. The $\text{H}_2$-MgO LJ interaction parameters are given by $\sigma = 2.014$ Å, $\epsilon = 45.91$ K [5]. The $\text{H}_2$-$\text{H}_2$ interaction potential was taken to be of the Silvera-Goldman form [125]. The system was studied numerically via the path integral Monte Carlo algorithm [127, 128]. Temperatures between $T = 0.5$ K and 3 K, radii between $R = 2$ and 7 Å, and densities of $\rho = (2.55 \times 10^{-3}/\text{Å})/R^2$ and $\rho = (7.13 \times 10^{-2}/\text{Å})/R^2$. (The densities correspond to choosing a fixed number $N = 1$ or $N = 28$ of particles in a simulation cell of radius $R$ and fixed length 125 Å, with periodic longitudinal boundary conditions.)

The results obtained were very similar for both densities and all ranges of temperature and radii studied. A representative plot of the $\text{H}_2$ radial density distribution and the pore potential is given in Fig. 3.20 for radii between $R = 2.5$ and 3.25 Å.

The lowest pore size depicted, $R = 2.5$ Å, is just beyond the transition point (2.45 Å for the tubular case) to an off-axis minimum, where the $\text{H}_2$ should switch from a 1D axial phase to a 2D cylindrical shell. This is reflected in the potential energy curve (Fig. 3.20), which is very shallow for $R = 2.5$ Å. Correspondingly, we see that at this radius the $\text{H}_2$ molecules are still concentrated on the axis. However, with a remarkably small increase in pore radius, by 0.25–0.5 Å, the distribution rapidly shifts to peak off axis, signifying the onset of the shell phase. It is interesting that the transition from axial to shell phases coincides in $R$ with the shift of the classical potential minimum from on- to off-axis, even in the presence of quantum effects and interparticle interactions. One expects larger effects of interactions at higher density.

It should be noted that the radii depicted in Fig. 3.20 are unphysically small for MgO pores of realistic size. We chose to study them despite this problem in order to theoretically study an axial to cylindrical shell transition in a pore geometry, which can only occur for small pores which are highly confining. In addition, there
**Figure 3.20.** H$_2$ radial probability density distribution (at $T = 0.5$ K, $\rho = (2.55 \times 10^{-3}/\text{Å})/R^2$) and MgO pore potential, for pore radii $R = 2.5, 2.75, 3.0, \text{and} 3.25$ Å, as functions of dimensionless radius $r/R$. (Radial densities near $r = 0$ are exaggerated due to finite size effects after normalizing the radial distribution by $1/(2\pi r)$ to obtain the probability density.)

are some systems of larger radii in which the first layer to be adsorbed becomes a rigidly bound film, confining a fluid phase to a very localized vicinity of the pore axis [153]. Such possibilities help to justify the study of quasi-1D fluids.

### 3.5.4 Large pore phenomena

Relatively few simulation studies have been carried out for quantum fluids in “typical” size nanotubes, $R \sim 0.6$ to $1$ nm. Path integral calculations of Gatica et al. [165] reported the behavior of H$_2$ over a limited range of $R$ at $T = 10$ K. One of the more interesting phenomena is the pore-filling transition, shown for H$_2$ in Fig. 3.21 [165]. At low $\mu$, all of the molecules are localized within a thin layer, at $r = 0.3$ nm, located near the distance of closest approach to the nanotube. Above a threshold value of $\mu$, the axial phase appears and grows rapidly with increasing $\mu$. This axial phase can be thought of as an independent 1D phase. A close analogy is the behavior of the second layer film of He or H$_2$ on the surface of graphite, often treated by assuming that the only role of the first layer is to provide a holding potential [166].
Analytical and numerical problems associated with matter in cylindrical geometry are often computationally demanding, motivating the use of simplifying models that (we hope) capture the essential physics. Recently, we have explored such a description of the shell phase; the model assumes that all particles are constrained to lie on a cylindrical surface, \( r = R \). One might expect that by varying \( R \) between \( R = 0 \) and \( R = \infty \), one interpolates smoothly between 1D and 2D behaviors. This is naïve; instead, an intriguing “anomaly” arises: a significant enhancement of the binding occurs when the diameter of the cylinder, \( d = 2R \), is comparable to the equilibrium separation \( r_{\text{min}} \) in the pair potential. The condition \( d \sim r_{\text{min}} \) corresponds (for LJ interactions) to \( \sigma/R \sim 1.7 \). Indeed, this argument does explain the \( R \) value corresponding to the maximum cohesive energy (seen in Fig. 3.22) of the “cylindrical liquids” \(^4\)He and \(^3\)He. The \(^3\)He case is perhaps the most dramatic, because its liquid state does not exist in either 1D or 2D, while the cylindrical liquid \(^3\)He is found to have cohesive energy as high as 1.26 K for \( R = 0.18 \) nm.

These are variational results, obtained with Jastrow and Slater-Jastrow wave functions for \(^4\)He and \(^3\)He, respectively. Qualitatively similar, enhanced binding

Figure 3.21. Pore-filling transition of \( \text{H}_2 \) in a tube of radius 0.6 nm, from Gatica et al. [165]. Results are densities as a function of \( r \) at 10 K and indicated chemical potentials.
behavior was found for related problems involving similar binding problems on a cylindrical surface: He or H₂ dimers, a crystalline lattice confined to a cylinder, and the virial coefficient of a classical fluid [167, 168, 169]. The origin of this general behavior is that two interacting particles can maximally exploit a divergent “specific area” when the interatomic separation is favorable. This occurs when the particles are on opposite sides of the cylinder, with separation $|\mathbf{r}_2 - \mathbf{r}_1| = d = r_{\min}$. The specific area is defined as the cylindrical area residing within a separation interval $[r, r + dr]$, divided by $dr$. For completeness, we note that analogous results for the dimer binding have been found by Aichinger et al., using both the simple model of confinement on a cylinder and more realistic study of dimers inside a nanotube [170, 171]. The optimal binding value found for $R$ is very different in the two cases.

**Acknowledgments**

We are grateful to our collaborators (Massimo Boninsegni, Louis Bruch, Mercedes Calbi, Carlo Carraro, Silvina Gatica, and Milen Kostov) for many contributions to this project and to NSF for its support of this research.
A.1 Thermal wavelength

A rule of thumb is that quantum effects become important when the interparticle spacing is less than or equal to the (de Broglie) thermal wavelength,

\[ \lambda = \frac{\hbar}{\sqrt{2\pi mT}} = \sqrt{\frac{\hbar}{mT/(2\pi)}} = \sqrt{\frac{2\pi^2 \hbar^2 \beta}{m}} \propto \frac{1}{\sqrt{mT}}. \]  

(A.1)

This condition may also be stated as the requirement that the particle density \( n = N/V \) exceed the “quantum concentration” \( n_Q \),

\[ n \gg n_Q, \quad n_Q \equiv \frac{1}{\lambda^D}, \]  

(A.2)

where \( D \) is the number of spatial dimensions.

The thermal wavelength \( \lambda \) physically represents, roughly speaking, the “quantum smeared size” of a point particle due to its quantum zero point motion. (This claim is justified rigorously by Eq. A.9.) The quantum concentration \( n_Q \) may be interpreted as the density of a system containing one particle per “particle-sized” volume of space. The constraint that \( n \) must exceed \( n_Q \) for quantum effects to become important then implies that quantum effects matter when there are multiple particles occupying a “particle-sized” volume of space (\( \lambda^D \)), i.e., their wavefunctions overlap to some significant extent. The zero-point motion is larger for small particle masses or low temperatures, so lighter or colder particles are “more quantum” in their behavior.

\(^1\)The quantum concentration for Fermi-Dirac systems sometimes has absorbed into its definition a degeneracy factor \( g \), expressing internal degrees of freedom such as spin; the definition of \( n_Q \) in Eq. A.2 is then multiplied by \( g \).
An order of magnitude estimate for the thermal wavelength scale proceeds by assuming that the particle energy is governed by the thermal scale, \( E_T \approx T \), leading to a thermal momentum of \( p_T = \sqrt{2mT} \), and by de Broglie’s relation, to an approximate thermal wavelength of \( \lambda_T = h/p_T = h/\sqrt{2mT} \), or in terms of the true thermal wavelength \( \lambda \), \( \lambda_T \approx 1.77 \lambda \). A similar calculation using \( E_g \approx D^2T \) for the average thermal energy of an ideal \( D \)-dimensional classical gas gives rise to an estimate for the thermal wavelength of \( \lambda_g = \sqrt{2\pi/D\lambda} \approx 1.45 \lambda \) (for \( D = 3 \)).

The actual thermal wavelength is derived from a more sophisticated analysis of statistical degeneracy, when the indistinguishable nature of quantum particles necessitates the use of quantum statistics instead of classical distinguishable statistics. The probability distribution for particles of energy \( E \) at fixed inverse temperature \( \beta \) and chemical potential \( \mu \) (i.e., the grand canonical ensemble) is given by

\[
p(E) \propto \frac{1}{z^{-1}e^{\beta E} + a}, \tag{A.3}
\]

where \( z = \exp(\beta \mu) \) is the fugacity. Setting \( a = 0 \) gives the Maxwell-Boltzmann distribution for classical (distinguishable) particles, \( a = +1 \) gives the Fermi-Dirac distribution for quantum (indistinguishable) fermions, and \( a = -1 \) gives the Bose-Einstein distribution for quantum bosons.

For quantum statistics, \( a = \pm 1 \). When \( z^{-1}e^{\beta E} \gg 1 \), Eq. A.3 reduces to the Maxwell-Boltzmann case, because \( a \) is negligible in comparison to the \( z^{-1}e^{\beta E} \) factor. Therefore, the classical limit is obtained when

\[
z = e^{\beta \mu} \ll e^{\beta E}. \tag{A.4}
\]

Since \( e^{\beta E} \geq 1 \), we can replace the above equation with the more conservative constraint that

\[
z \ll 1, \tag{A.5}
\]

for the classical limit to obtain.

To relate this constraint to the quantum concentration, we note that the average particle number is given by

\[
N = \int dE \frac{g(E)}{z^{-1}e^{\beta E} + a}, \tag{A.6}
\]

where \( g(E) \) is the density of states. For the Maxwell-Boltzmann distribution this evaluates to

\[
N_{MB} = \frac{V}{\lambda^D z}, \tag{A.7}
\]

so that \( z = n/n_Q \). The classical limit \( z \ll 1 \) then becomes \( n/n_Q \ll 1 \), which is equivalent to the condition for the onset of quantum behavior given in Eq. A.2.²

²The foregoing derivation was inspired by the discussion in Kelly \cite{172}.
The Bose-Einstein and Fermi-Dirac cases give rise to more complicated formulas with polylogarithms, but a small-$z$ expansion of $N_{BE}$ and $N_{FD}$ reduces to $N_{MB}$ in both cases to lowest order, and the same result obtains in this approximation.

The claim that the thermal wavelength of its particle represents its quantum zero point motion is justified heuristically by the prior appeal to the de Broglie wavelength $\lambda = h/p$, but it can be made more precise. The density matrix $\hat{\rho}$ of a quantum statistical system is governed by an imaginary-time Schrödinger (or diffusion) equation ([133], §2.3). For a free particle its “time evolution” is given in the position representation by ([118], §5.3; [133], §2.4),

$$-\frac{\partial \hat{\rho}}{\partial \beta} = \frac{\hbar^2}{2m} \nabla^2 \hat{\rho}.$$ (A.8)

where $\rho(x)$ is the density matrix of a particle propagating from the origin to a position $x$. We further stipulate that the particle is confined to a $D$-dimensional box of volume $V$. The solution of this equation, upon normalizing the partition function to unity to determine the constant of proportionality, is a Gaussian:

$$\rho(x) = \frac{1}{V} \exp \left[-\frac{1}{2} |x|^2 / \lambda_0^2 \right], \quad \lambda_0 = \lambda / \sqrt{2\pi}.$$ (A.9)

The “zero point wavelength” $\lambda_0$ is the standard deviation of a free particle undergoing quantum fluctuations from its average position and is thus a direct measure of its zero point motion.

In this sense $\lambda_0$ may be a more natural physical measure of the “quantumness” of a particle than is $\lambda$, and some references call $\lambda_0 \approx 0.4\lambda$ the “thermal wavelength” [127]. The definition used here was chosen because $\lambda$ appears naturally in thermodynamic equations involving classical and quantum ideal gases, such as the particle number (Eq. A.7) and the partition function itself, as well as in the virial expansion which is expressed in powers of $n/n_Q$.

Still another measure of the “quantum size” of a particle is given by the effective potential arising from the path integral representation of quantum statistical mechanics (discussed more fully in Section 3.2.1). The classical statistical mechanics of noninteracting particles is governed by the Boltzmann factor, which depends on the external potential. Path integrals give rise to a semiclassical approximation in which the quantum statistical mechanics of noninteracting particles is given by an effective potential, which is approaches the classical potential in the classical limit but contains quantum corrections. The lowest order approximation to this effective potential is given by the classical potential “quantum smeared” by convolving it with a Gaussian of standard deviation $\lambda_e \equiv \lambda_0 / \sqrt{12}$. The “semiclassical effective thermal wavelength” $\lambda_e$ determines, in this context, the spatial extent over which quantum mechanical fluctuations “smear” a classical point particle.

---

$^3Z = (V/\lambda^D)^N/N!$ in the canonical ensemble.
In Eq. A.9, describing the quantum mechanics of a free particle, we can see the role of the thermal wavelength in many-body quantum statistics as well, albeit in terms of $\lambda_0$ instead of $\lambda$. It is easier to ignore normalization constants, so we begin with the unnormalized version of the free particle density matrix (Eq. A.9), $\rho_U^{(1)}(x)$, where the notation $\cdots^{(1)}$ emphasizes that a single particle is involved:

$$\rho_U^{(1)}(x) = \frac{1}{\lambda^D} \exp \left[ -\frac{1}{2} \frac{|x|^2}{\lambda_0^2} \right], \quad (A.10)$$

where $\rho_U^{(1)} = \exp(-\beta \hat{H}^{(1)})$, so that $\hat{\rho}^{(1)} = \rho_U^{(1)}/Z$, $Z = \text{tr} \rho_U^{(1)}$.

In order to study the effects of quantum exchange statistics, we need to examine the statistics of a gas of particles, rather than that of a single particle. The generalization of the free particle is the $N$-particle noninteracting gas. The diagonal elements of the $N$-particle density matrix $\hat{\rho}_U^{(N)}$ in the position representation are a product of $N$ free particle density matrices summed over all permutations $P$ (Pathria [118], §5.5):

$$\langle x_1, \ldots, x_N | \rho_U^{(N)} | x_1, \ldots, x_N \rangle = \frac{1}{N!} \sum_P (\pm 1)^{|P|} \prod_i \rho_U^{(1)}(P x_i - x_i), \quad (A.11)$$

where $P x$ denotes the permutation of a particle coordinate vector into another coordinate vector, $[P]$ is the order of the permutation, and $(\pm 1)^{|P|}$ takes the $+$ sign for Bose-Einstein symmetric particle exchange and the $-$ sign for Fermi-Dirac antisymmetric particle exchange.

Continuing the development of Pathria [118], the sum over permutations can be grouped in terms of sums over zero, one, two, … pair exchanges,

$$\sum_P = 1 \pm \sum_{i<j} \rho_U^{(1)}(x_i-x_j)\rho_U^{(1)}(x_j-x_i) + \sum_{i<j<k} \rho_U^{(1)}(x_i-x_j)\rho_U^{(1)}(x_j-x_k)\rho_U^{(1)}(x_k-x_i) \pm \cdots, \quad (A.12)$$

Because $\rho_U^{(1)}(x)$ decays exponentially with characteristic length $\lambda_0$, the higher order terms become negligible when the interparticle spacing is large compared to the zero-point thermal motion of an individual particle, $|x_i-x_j| \gg \lambda_0$. The only surviving term is the leading zeroth order term representing the identity permutation—in other words, the classical case of distinguishable particles when no exchange takes place. This is equivalent to $N/V \ll 1/\lambda^D$, or $n \ll n_Q$, the same condition derived above.

The effects of quantum statistical degeneracy are directly visible in typical particle paths sampled from path integral Monte Carlo simulations. When the number density of the system grows comparable to the quantum concentration, the wavefunctions of neighboring particles can significantly overlap due to the uncertainty in position as characterized by $\lambda_0$; the probability of particle exchange becomes significant. In $^4$He, the multiparticle exchanges that take place can span
Figure A.1. Typical paths of six $^4$He atoms in $D = 2$, from path integral Monte Carlo simulations. Left: Normal fluid helium at $T = 2$ K ($n/n_Q = 6.3$, $\lambda_0 = 2.5$ Å). Right: Superfluid helium at $T = 0.75$ K ($n/n_Q = 16.9$, $\lambda_0 = 4.0$ Å). Visible are multiparticle paths spanning the entire system, arising from statistical degeneracy due to particle exchange at high number density relative to the quantum concentration. (Note: computed here are the 2-dimensional number density and quantum concentration, $n/n_Q = N\lambda^2/A$.) [Source: David M. Ceperley [127].]

<table>
<thead>
<tr>
<th>ad</th>
<th>$\lambda\sqrt{\frac{T}{\text{[Å} \cdot \sqrt{\text{K}]}}}$</th>
<th>$\lambda_0\sqrt{\frac{T}{\text{[Å} \cdot \sqrt{\text{K}]}}}$</th>
<th>$\lambda_e\sqrt{\frac{T}{\text{[Å} \cdot \sqrt{\text{K}]}}}$</th>
</tr>
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</tr>
<tr>
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<td>1.55</td>
<td>0.44</td>
</tr>
<tr>
<td>Ar</td>
<td>2.76</td>
<td>1.10</td>
<td>0.32</td>
</tr>
<tr>
<td>Kr</td>
<td>1.91</td>
<td>0.76</td>
<td>0.22</td>
</tr>
<tr>
<td>Xe</td>
<td>1.52</td>
<td>0.61</td>
<td>0.18</td>
</tr>
</tbody>
</table>

Table A.1. Thermal wavelength $\lambda = \sqrt{\frac{2\pi\hbar^2\beta}{m}} = (17.458$ Å $\cdot \sqrt{\text{amu-K}})/\sqrt{mT}$, zero point thermal wavelength $\lambda_0 = \lambda/\sqrt{2\pi} = (6.965$ Å $\cdot \sqrt{\text{amu-K}})/\sqrt{mT}$, and semiclassical effective thermal wavelength $\lambda_e = \lambda_0/\sqrt{12} = (2.011$ Å $\cdot \sqrt{\text{amu-K}})/\sqrt{mT}$, for various adsorbates.

the entire size of the system, leading to superfluidity. This scenario is depicted in Figure A.1.

The thermal wavelengths for various adsorbates are given in Table A.1. Generalizations of some of the results in this appendix may be found in Yan [173] and Barker et al. [174].
A.2 Heat capacity

A.2.1 Fluctuation formulas

The (isochoric) heat capacity is the rate of change of energy with temperature at constant system volume and particle number,

\[ C_V(T) \equiv \frac{\partial E}{\partial T}_{N,V} \tag{A.13} \]

In the canonical ensemble, it can also be written in terms of energy fluctuations,

\[ C_V(T) = \left\langle \left( \frac{\delta E}{T} \right)^2 \right\rangle = \frac{\langle E^2 \rangle - \langle E \rangle^2}{T^2} , \quad \delta E \equiv E - \langle E \rangle . \tag{A.14} \]

where \( \langle \cdot \rangle \) denotes an expectation value in the canonical ensemble. This formula can be derived from the partition function,

\[ Z = \sum_i \exp (-\beta E_i) . \tag{A.15} \]

Denoting the \( \beta \) derivative of \( Z \) by \( Z' = \partial Z / \partial \beta \), it is easy to show that

\[ E \equiv \langle E \rangle \equiv Z^{-1} \sum_i E_i \exp (-\beta E_i) = -\frac{Z'}{Z} . \tag{A.16} \]

Similarly, it can be shown that

\[ \langle E^2 \rangle = \frac{Z''}{Z} . \tag{A.17} \]

Since \( C_V = \partial E / \partial T = -\beta^2 \partial E / \partial \beta \), we find

\[ C_V = -\beta^2 \times \left[ \frac{Z''}{Z} - \left( \frac{Z'}{Z} \right)^2 \right] = \beta^2 (\langle E^2 \rangle - \langle E \rangle^2) , \tag{A.18} \]

which is equivalent to Eq. A.14.

A similar procedure can be followed to derive a corresponding fluctuation formula in the grand canonical ensemble. The details are more tedious; the reader should consult the discussion in Pathria ([118], §4.5) or the more elegant and complete derivation in Planes and Vives ([175]); the canonical ensemble expression \( C_V = \beta^2 \langle \delta E^2 \rangle \) is replaced by

\[ C_V(\beta) = \beta^2 \left[ \langle \delta E^2 \rangle - \frac{\langle \delta E \delta N \rangle}{\langle \delta N^2 \rangle} \right] , \tag{A.19} \]

where \( \langle \cdot \rangle \) here denotes expectation values taken in the grand canonical ensemble, and \( \delta E \equiv E - \langle E \rangle , \delta N \equiv N - \langle N \rangle \).
A.2.2 Two-state systems: Schottky anomaly

At sufficiently low temperatures, a quantum system with a discrete energy spectrum can be approximated by a two state system, given by its ground state and first excited state, since there will not be enough thermal energy to excite the system to higher energy states. (This assumes that the system is fully quantized, i.e., there are no continuum levels in the energy spectrum.) A two state system then becomes an appropriate model system and test case against which low temperature results may be compared.

Assume that the ground state is nondegenerate with energy \( E = 0 \), and the excited state has degeneracy \( g \) with energy \( E = \epsilon \). Ignoring quantum statistics (i.e., Maxwell-Boltzmann statistics) and working within the canonical ensemble, the partition function of the two state system is

\[
Z = 1 + ge^{-\beta \epsilon}.
\]  

(A.20)

The average energy of the system is

\[
E = -\frac{\partial}{\partial \beta} \ln Z = \frac{g \epsilon e^{-\beta \epsilon}}{1 + ge^{-\beta \epsilon}}.
\]  

(A.21)

The heat capacity is

\[
C_V = -\beta^2 \frac{\partial E}{\partial \beta} = \frac{g \beta^2 \epsilon^2 e^{-\beta \epsilon}}{1 + ge^{-\beta \epsilon}} = (\beta E)^2 e^{\beta \epsilon} / g.
\]  

(A.22)

When the excited state is nondegenerate \((g = 1)\), these equations simplify to

\[
E = \frac{\epsilon}{2} \left( 1 - \tanh \frac{\beta \epsilon}{2} \right),
\]  

(A.23)

\[
C_V = \left( \frac{\beta \epsilon}{2} \text{sech} \frac{\beta \epsilon}{2} \right)^2.
\]  

(A.24)

The temperature dependence of the heat capacity is depicted in Figure A.2; it vanishes at low and high temperature when all the particles are in the ground or excited state, respectively, but attains a maximum at an intermediate temperature where substantial promotion from the ground to the excited state takes place. This peak in \( C_V(T) \) is referred to as the Schottky anomaly.

The maximum heat capacity can be determined numerically. For \( g = 1 \), it occurs at \( T/\epsilon = 0.417 \), \( C_V = 0.439 \). The location of the peak at \( T \approx 0.4\epsilon \) gives rise to the “2/5 rule” of thumb, which says that the heat capacity is enhanced when the thermal energy becomes approximately two-fifths of some characteristic excitation energy in the system. For \( g = 2 \), the peak is at \( T/\epsilon = 0.377 \), \( C_V = 0.762 \). This peak is at a lower temperature and is greater in magnitude than the nondegenerate \((g = 1)\) peak, reflecting the fact that it is easier to excite the system into a higher state when there are more states into which the system can be excited.
Figure A.2. Heat capacity peak (Schottky anomaly) in a classical two-state system, as a function of dimensionless temperature $T/\epsilon$, where $\epsilon$ is the excitation gap. Depicted are the cases of a nondegenerate ($g = 1$) and doubly degenerate ($g = 2$) excited state (with a nondegenerate ground state).

These calculations can be repeated for a two-state system in which the particles obey Bose-Einstein quantum statistics. In this case, the mean occupation numbers of the ground and excited states are

\[ N_0 = \frac{1}{z^{-1} - 1} = \frac{z}{1 - z}, \quad (A.25) \]

\[ N_1 = g \frac{1}{z^{-1} e^{\beta \epsilon} - 1} = \frac{gz}{e^{\beta \epsilon} - z}, \quad (A.26) \]

where $z = e^{\beta \mu}$ is the fugacity. Imposing the constraint that the average particle number of the system must be fixed, $N = N_0 + N_1$, the fugacity may be determined analytically,\(^4\)

\[ z = \frac{g + N + (1 + N)e^{\beta \epsilon} - \sqrt{(g + N + (1 + N)e^{\beta \epsilon})^2 - 4N(1 + g + N)e^{\beta \epsilon}}}{2(1 + g + N)}. \quad (A.27) \]

\(^4\)Superficially, there are multiple solutions for $z$, but the correct solution may be singled out by imposing the constraints that $N_0, N_1 > 0$. 
Figure A.3. Heat capacity peak (Schottky anomaly) in a quantum two-state system obeying Bose-Einstein statistics, as a function of dimensionless temperature $T/\epsilon$, where $\epsilon$ is the excitation gap. Depicted are the cases of a nondegenerate ($g = 1$) and doubly degenerate ($g = 2$) excited state (with a nondegenerate ground state). Superimposed are the heat capacity curves for various numbers of particles: (from largest peak to smallest) $N = 1, 5, 10, \text{and } 30$; also shown are the classical results from Figure A.2.

The average energy is then $E = 0 \cdot N_0 + \epsilon \cdot N_1 = \epsilon N_1$, or

$$E/\epsilon = \frac{g \{ g + N + (1 + N)e^{\beta\epsilon} - \sqrt{(g + N + (1 + N)e^{\beta\epsilon})^2 - 4N(1 + g + N)e^{\beta\epsilon}} \}}{(1 + 2g + N)e^{\beta\epsilon} - g - N - \sqrt{(g + N + (1 + N)e^{\beta\epsilon})^2 - 4N(1 + g + N)e^{\beta\epsilon}}}.$$

(A.28)

The heat capacity obtained by differentiating the energy with respect to temperature, for which the analytic expression is obviously unwieldy, is given in Figure A.3.

Unlike the classical case, the quantum heat capacity depends on the number of particles in the system, since the “gregarious” nature of bosons means that particles already in the ground state will “attract” other particles into the ground state.\(^5\) Accordingly, the heat capacity due to promotion out of the ground state will be delayed in temperature and diminished when large numbers of particles are present, hindering excitation.

\(^5\)It is tempting but ultimately incorrect to treat Bose-Einstein statistics as an attractive “statistical exchange force” [176].
Monte Carlo simulation

B.1 Overview

This section gives an informal overview of Monte Carlo methods, including Monte Carlo integration (importance sampling) and Monte Carlo simulation (Markov Chain Monte Carlo), including the Metropolis algorithm.

B.1.1 Introduction

Monte Carlo is the art of approximating an expectation [value] by the sample mean of a function of simulated random variables.¹

Consider integration. Recall how we approximate an integral by a Riemann sum:

\[
\int_a^b f(x) \, dx \approx \sum_i f(x_i) \Delta x = \sum_i f(x_i) \frac{b-a}{N}.
\]

In the Riemann sum, the \( x_i \) are spaced uniformly in the interval \((a, b)\). But if we choose them to be random numbers drawn uniformly from \((a, b)\) instead, we get pretty much the same result.

To see why, compare it to the formula for the expectation value of a function,

\[
\langle f \rangle = \int f(x)p(x) \, dx,
\]

where \( f(x) \) is an observable and \( p(x) \) is the probability distribution function (pdf) of \( x \). Over an interval \((a, b)\), the uniform distribution is \( p(x) = 1/(b-a) \) (since it is constant and \( \int_a^b p(x) \, dx = 1 \)). Thus, we can interpret \( \int_a^b f(x) \, dx \) as the expectation

¹Attrib.: Eric C. Anderson.
\[(b - a)f = \int_a^b f(x)(b - a)p(x) \, dx\] taken with respect to the uniform probability distribution, which may be approximated by the sample mean \((b - a)\sum f(x_i)/N\).

We know from statistics that if we draw \(N\) random numbers \(x_i\) from a pdf \(p(x)\), then as \(N \to \infty\), the sample mean \(\bar{f} = \sum f(x_i)/N\) approaches the true expectation \(\langle f \rangle\). This justifies the earlier claim that we can do a “Riemann sum” by choosing the \(x_i\) to be random instead of evenly spaced, and still get a good approximation to the integral.

The question arises: why go to the effort of generating random numbers, when you can use evenly spaced numbers instead? And what is the use of pretending an integral is an expectation value?

In fact, paraphrasing Alan Sokal\(^2\) and Winston Churchill,\(^3\)

> “Monte Carlo is the worst integration algorithm there is, except for all the others.”

### B.1.2 Monte Carlo integration

#### B.1.2.1 Importance sampling

If one takes the Riemann sum of a function that is highly peaked, like \(f(x) = \exp(-x^2)\), much time will be wasted calculating \(f(x_i)\) for points far away from the peak that don’t contribute much to the overall integral. But if one instead drew the \(x_i\) randomly from a Gaussian distribution, most of them will be near the central peak in \(f(x)\). To get the same accuracy of estimate for the integral, we can get by with fewer points than a Riemann sum—or we can use the same number of points and get better accuracy.\(^4\)

Note that Monte Carlo integration is only going to be helpful if you have a way of drawing numbers from a pdf \(p(x)\). Uniform random number generators are easy to come by, but can we generate numbers with, say, a Gaussian distribution? There is a trick called the Box-Muller transformation which will produce a pair of Gaussian random numbers from a pair of uniform random numbers on \((0, 1)\). But we cannot rely on being able to generate random numbers for any distribution. (Actually, we can, in Markov Chain Monte Carlo; that will come later.) What can we do?

Suppose we want to integrate the Maxwellian distribution \(f(x) = x^2 \exp(-x^2)\) over some interval \((a, b)\).\(^5\) We could use the uniform pdf \(p(x) = 1/(b - a)\) as in

\(^{2\text{“Monte Carlo is an extremely bad method; it should be used only when all alternative methods are worse.” [177]}}\)

\(^{3\text{“Democracy is the worst form of government, except for all those others that have been tried.”}}\)

\(^{4\text{I haven’t actually checked if a Gaussian is peaked enough for importance sampling to be superior to Riemann sums, Simpson’s rule, etc. The basic idea, however, is valid.}}\)

\(^{5\text{Here we are neglecting normalization in pdfs for convenience from now on. In Markov Chain Monte Carlo, normalization will turn out to be unnecessary anyway.}}\)
Eq. B.2, but then we would be wasting points spread over parts of the interval away from the peak, just like in the Riemann sum example. We could try drawing from the distribution \( p(x) = x^2 \exp(-x^2) \) directly, but there is not an obvious way of drawing random numbers from an arbitrary distribution.

But we do know how to draw Gaussian random numbers. So we can write \( f(x) = g(x)p(x) \) where \( g(x) = x^2 \) and \( p(x) = \exp(-x^2) \). Then

\[
\int_a^b f(x) \, dx = \int_a^b g(x)p(x) \, dx = \langle g \rangle = \langle x^2 \rangle ,
\]

where the expectation is taken with respect to the pdf \( p(x) = \exp(-x^2) \). So we can draw our \( x_i \) from a Gaussian, which we know how to do. While a Gaussian is not as peaked as the Maxwellian itself, it is still better than uniform sampling: we spend more time in the important parts of the integrand.

### B.1.2.2 Multidimensional integration

Even if our integrand is not sharply peaked, deterministic integration methods like Simpson’s rule are still not necessarily the best. In an integral of dimension \( d \), the number of grid points necessary to uniformly span a volume \( L^d \) grows like \( N^d \) if we want to maintain a constant grid density in each dimension. For a large number of dimensions, this adds up to quite a few grid points. It turns out that the error in Simpson’s rule for a given number of grid points scales like \( \epsilon \sim N^{-4/d} \) [177]. Monte Carlo integration error, on the other hand, scales like \( N^{-1/2} \) (the standard \( 1/\sqrt{N} \) error formula for \( N \) measurements). For \( d < 8 \), Simpson’s rule gives more accuracy for a given number of points, but for \( d > 8 \), Monte Carlo is better. (These are rough estimates. The constant of proportionality in front of the scaling law matters.)

In fact, for high dimensions, Monte Carlo is the only feasible integration algorithm. Consider the partition function of a statistical mechanics system with hundreds or thousands of particles, each described by three position variables. Or a lattice chromodynamics calculation, integrating over field configurations specified on the links of spacetime lattices: a problem typically with on the order of a million variables over which to integrate. Monte Carlo provides the only direct computational method for these problems.

### B.1.3 Markov Chain Monte Carlo simulation

In Sec. B.1.2.1, we wanted to draw from a highly peaked pdf \( p(x) = x^2 \exp(-x^2) \), but we had no way of drawing random numbers from an arbitrary distribution. We settled for drawing them from a less highly peaked distribution \( p(x) = \exp(-x^2) \), because we do know how to generate Gaussian random numbers. Finding a “nice” pdf becomes problematic with complicated or high-dimensional integrands. It
would be better if we could generate random numbers from any probability distribution.

The Markov Chain Monte Carlo (MCMC) algorithm, or “Monte Carlo simulation”, provides a method to draw samples from an arbitrary pdf. It works by random walk: to go from sample \( x_i \) to \( x_{i+1} \), one wanders randomly around the domain for a while, taking uniform steps back and forth, and then takes another sample. The trick is to bias the direction of the random walk, since a random walk that is unbiased in any direction will diffuse into a Gaussian distribution. Biasing the walk so that some directions are more probable than others allows the random walk to diffuse to an arbitrary pdf. It is called “Markov chain” Monte Carlo because a random sequence in which the \((i+1)\)th sample depends only on the \(i\)th sample is known as a Markov chain.

The bias in the random walk is represented by a transition function \( t(x', x) \), the probability that a walker at point \( x \) will end up at point \( x' \). It turns out that a sufficient condition for a random walk to diffuse to an arbitrary pdf \( p(x) \) over a long period of time is the detailed balance condition—a transition from \( x \) to \( x' \) should be equally probable as a transition from \( x' \) to \( x \): \( t(x', x) = t(x, x') \).\(^6\)

We can write the transition probability in terms of conditional probabilities: the probability that we transition \( x \rightarrow x' \) is given by \( t(x', x) = a(x', x)p(x) \), where \( p(x) \) is the probability that we are in state \( x \) to begin with, and \( a(x', x) \) is the conditional “acceptance probability”, i.e., the probability that we are in state \( x \) and then accept a proposed move from \( x \) to \( x' \). Then detailed balance becomes,

\[
a(x', x) p(x) = a(x, x') p(x') .
\]

To produce an appropriately biased transition function, we need to produce an appropriately biased acceptance probability. To satisfy detailed balance we can choose any function satisfying Eq. B.4.

The Metropolis algorithm \(^{103}\) is defined by what is probably the simplest choice for an acceptance probability:

\[
a(x', x) = \begin{cases} 
1, & p(x') > p(x) \\
\frac{p(x')}{p(x)}, & p(x') < p(x) .
\end{cases}
\]

(Exercise: verify that this satisfies Eq. B.4.) We can see that in the Metropolis algorithm, normalizing pdfs is unnecessary, because only ratios of probabilities influence the random walk: normalization constants cancel out.

\(^6\)It is not actually sufficient by itself—we also need ergodicity: the transition probabilities must be such that it is possible to ultimately reach any point from any other.
Accordingly, the Metropolis MCMC algorithm is:

1. Starting at some point $x_i$:
   
   (a) Propose a move to a new point a (uniform) random displacement $\delta$ away: $x' = x + \delta$.
   
   (b) Accept this move (“step”) with probability $a(x', x)$, else reject the move and remain at point $x$. (Either way, this counts as “performing a move”.)

2. Repeat the propose-accept/reject “update” loop many times until the state has diffused (walked) through the domain sufficiently to produce a statistically independent new sample $x_{i+1}$; record (“measure”, “sample”) this new point (and the values of any observables to be measured).

Once a set of $N$ random points $x_i$ has been obtained, expectation values can be calculated by $\langle f \rangle = \sum_i f(x_i)/N$.

### B.1.3.1 Example: Statistical mechanics

In statistical mechanics, we want to calculate expectation values of observables with respect to the Boltzmann distribution, $p(x) = \exp[-\beta E(x)]/Z$, where $Z = \int \exp[-\beta E(x)] \, dx$ is the partition function and $x$ is a configuration (microstate) vector (3$n$ dimensional for $n$ particles).\(^7\) In Monte Carlo simulation we often ignore the kinetic energy and take $E = U$, since the kinetic energy can be integrated out analytically via the equipartition theorem.

Given the Boltzmann form for the pdf, the Metropolis acceptance criterion becomes,

$$a(x', x) = \begin{cases} 
1, & \Delta E < 0 \\
\exp(-\beta \Delta E), & \Delta E > 0 
\end{cases} \quad \text{(B.6)}$$

We always accept moves to lower energies, but climb to higher energies with a probability that decreases with increasing energy.

A common model system to study Monte Carlo is the 2D classical Ising model, a square lattice of $n \times n$ spins $\sigma_{ij}$ that are either up or down ($\sigma_{ij} = \pm 1$). Assuming that each spin is coupled to each of their four nearest neighbors with energy $\pm J$ for (anti)parallel spins, its Hamiltonian is given by,

$$E = -J \sum_{i=1}^{N} \sum_{j=1}^{N} \sigma_{ij} (\sigma_{i-1,j} + \sigma_{i+1,j} + \sigma_{i,j-1} + \sigma_{i,j+1}) \quad \text{(B.7)}$$

\(^7\)We don’t actually have to calculate the partition function, since it is a normalization constant.
(The $J/2$ corrects for double-counting each spin-spin coupling. To avoid having to deal with boundary conditions, we usually take the lattice to be a torus by identifying opposite edges of the squares, so that all indices are modulo $N$.)

This is a good test system because it is simple, it has interesting physics (a second-order phase transition at a critical temperature $T_c$), and its exact solution is known. The critical temperature, energy per spin, and specific heat (heat capacity per spin) can be obtained by Onsager’s solution and are given by ([118], §12.3)

\[ k_B T_c = \frac{2}{\ln (1 + \sqrt{2})} J \approx 2.27J, \]  
\[ E/N^2 = -J \coth (2K) \left\{ 1 + \frac{2\kappa'}{\pi} K_1(\kappa) \right\}, \]  
\[ C_V/(N^2 k_B) = \frac{2}{\pi} (K \coth (2K))^2 \left[ 2\{K_1(\kappa) - E_1(\kappa)\} - (1 - \kappa') \left\{ \frac{\pi}{2} + \kappa' K_1(\kappa) \right\} \right], \]

where $K = \beta J$, $\kappa = 2 \sinh (2K)/\cosh^2 (2K)$, $\kappa' = 2 \tanh^2 (2K) - 1$, $K_1(\kappa) = \int_0^{\pi/2} d\phi/\sqrt{1 - \kappa^2 \sin^2 \phi}$, and $E_1(\kappa) = \int_0^{\pi/2} d\phi \sqrt{1 - \kappa^2 \sin^2 \phi}$. The energy per spin at the critical temperature is $-\sqrt{2}J \approx -1.414J$, and the heat capacity diverges (second order phase transition).

The exact Onsager solution as well as Monte Carlo simulations are depicted in Fig. B.1. The MCMC code which generated the simulation data is listed in Sec. B.1.3.3.

### B.1.3.2 Caveats

The following are points to watch out for in Monte Carlo simulation:

**Random number quality.** Not all random number generators are created equal.

**Equilibration.** The random walk must go through an “equilibration”, “thermalization”, or “burn-in” time before it starts to converge to the target distribution $p(x)$; some of the initial samples must be discarded.

**Correlation.** In between measurements (samples), enough moves must be made that two successive samples are statistically independent; the number of moves must exceed the “autocorrelation time” between moves. Near second order phase transitions, the autocorrelation time diverges (because the physical correlation length diverges)—this is known as “critical slowing down”—so it is hard to probe these transitions using (naïve) MCMC.

**Rejection.** Sometimes so many moves are rejected that it takes a very long time to achieve decorrelation.
Ergodicity. The transitions must be ergodic (sample all of configuration space).
It is possible to get trapped for a long time in metastable states (e.g., near first order phase transitions); the simulation exhibits hysteresis (samples are not independent of where the random walk starts).

Finite size effects. Simulated systems are not truly infinite so there is no thermodynamic limit, strictly speaking; divergences are softened into finiteness, smaller systems do not reflect infinite system behavior. By examining how physical quantities scale with increasing system size (finite size scaling), the thermodynamic limit may be extrapolated.

There are many variations on the simple algorithm described here that overcome these problems.

B.1.3.3 Code listing (2D Ising MCMC)

Below is the C++ listing for ising2d.cpp, a Markov Chain Monte Carlo simulation of the classical 2D Ising model. The code may be compiled with g++ -o ising2d ising2d.cpp, and executed with ./ising2d T where T is the dimensionless temperature $k_B T/J$. It outputs a line with three numbers: $k_B T/J$, $E/(N^2 J)$, and $C_V/(N^2 k_B)$. (Internally it uses units where $k_B = J = 1$.) The system size is hardcoded to $N = 32$ but may be modified.

If the output of a number of runs at different temperatures is combined into one file, with one run output per line, the temperature dependence of $E/(N^2 J)$ can be plotted with the command echo 'plot "filename" u 1:2' | gnuplot -persist (change the 1:2 to 1:3 for $C_V/(N^2 k_B)$).

These instructions are for Unix/X11.

```c++
// 2D Ising model via Metropolis Markov Chain Monte Carlo
// Nathan Urban (nurban@phys.psu.edu)
// H = -J sum_{ij} S_{ij} (sum_{"nearest neighbors"} S_{n.n.})
// (units where k_B = J = 1; replace E->E/J, T->k_B T/J)

#include <iostream.h> // or #include <iostream>
#include <math.h>
#include <stdlib.h>
#include <time.h>

const int N=32;
long E = -2*N*N; double Etot=0.0, E2tot=0.0;
double T;
int spin[N][N];

inline double rnd(void) {return random()/2147483647.;}
```
// assuming MAXINT=2^31−1

void update(void)
{
    // propose move (site to flip)
    int i = int(rnd() * N); int j = int(rnd() * N);

    // energy shift
    int dE = 2 * spin[i][j] * ( spin[(i+N−1)%N][j] + spin[(i+1)%N][j] + spin[i][(j+N−1)%N] + spin[i][(j+1)%N] );

    if( dE < 0 || rnd() < exp(−dE/T) ) { // Metropolis test
        spin[i][j] = −spin[i][j]; // accept the move
        E = E + dE;
    }
}

void simulate(int numMeasurements, int updatesPerMeasurement, int skipUpdates)
{
    // equilibrate: discard 'skipUpdates' moves
    for(int u=0; u<skipUpdates; u++)
        update();
    for(int m=0; m<numMeasurements; m++) {
        for(int u=0; u<updatesPerMeasurement; u++)
            update();
        Etot = Etot + double(E); E2tot = E2tot + double(E*E);
    }
}

void initialize(void)
{
    // seed random number generator with the current time
    srandom(time(0));

    // initialize spin lattice to all spins up
    for(int i=0; i<N; i++)
        for(int j=0; j<N; j++)
            spin[i][j] = 1;
}
void output(int M)
{
    // average $<E>$ and $<E^2>$
    double Eavg = Etot/M; double E2avg = E2tot/M;
    // heat capacity $C_V = (E^2 - <E>^2)/T^2$
    double CV = (E2avg-Eavg*Eavg)/(T*T);

    // print temperature, energy per spin, specific heat
    cout << T << " " << Eavg/(N*N) << " "
         << CV/(N*N) << endl;
}

int main(int argc, char* argv[])
{
    // output usage message if not called with one argument
    if(argc != 2) {
        cerr << "Usage: " << argv[0] << " T " << endl;
        exit(1);
    }

    T = atof(argv[1]);
    initialize();

    int numMeasurements = 10000;
    simulate(numMeasurements,10*N*N,20*N*N);

    output(numMeasurements);
}
Figure B.1. Average energy per spin and specific heat (heat capacity per spin) for the 2D classical Ising model, for various lattice sizes $N \times N$. Continuous curves are the exact Onsager solution. Symbols are numerical estimates, each computed from $10^4$ samples of Metropolis MCMC simulation, with $20N^2$ equilibration moves and $10N^2$ moves between samples. The 2D Ising critical temperature is $T_c \approx 2.27J/k_B$. 
B.2 Metropolis Monte Carlo

See Section B.1.3, particularly Eq. B.5 and the subsequent description.

B.3 Wang-Landau Monte Carlo

See Sections 2.3.2 and 2.5.2, and the discussion at the end of Sec. 2.4.

B.4 Path integral Monte Carlo

Quantum systems can be simulated via the path integral Monte Carlo (PIMC) method. The canonical review of PIMC simulation in condensed matter is Ceperley [127]; the discussion below follows the development found there.

The path integral approach to quantum statistical mechanics [133] utilized by path integral Monte Carlo simulation [127] exploits the following $M$-fold factorization of the partition function in the position representation,

\[ Z = \text{tr} \hat{\rho} = \int dR \langle R | \hat{\rho} | R \rangle = \int dR \int dR_1 dR_2 \cdots dR_M \langle R | \hat{\rho}^{1/M} | R_1 \rangle \langle R_1 | \hat{\rho}^{1/M} | R_2 \rangle \times \cdots \times \langle R_{M-1} | \hat{\rho}^{1/M} | R_M \rangle \langle R_M | \hat{\rho}^{1/M} | R \rangle, \]

where $\hat{\rho} = \exp(-\beta \hat{H})$ is the unnormalized density matrix and $(R, R_1, \ldots, R_{M-1}, R)$ are the position coordinates of an $M$-step discretized, closed path in configuration space, beginning and ending at position $R$.\footnote{In the interests of notational simplicity, this expression ignores the permutation symmetry necessary to describe quantum statistical exchange.} In the limit that $M \to \infty$, this expression becomes an imaginary time path integral over closed, continuous paths; the discretized positions are referred to as “time slices”. (See Fig. A.1 for a depiction of paths sampled from a PIMC simulation.)

Path integral Monte Carlo simulation operates by drawing samples from the probability distribution defined by the integrand of Eq. B.11; the domain of the distribution consists of closed, discretized particle paths (worldlines), rather than of particle positions as in classical Monte Carlo.

It may not be obvious how the above factorization facilitates Monte Carlo simulation. The density matrix $\hat{\rho}$ is not easy to calculate. However, $\hat{\rho}^{1/M}$ is easier to calculate, if $M$ is large: we can write

\[ \hat{\rho} = e^{-\beta \hat{H}} = (e^{-\tau \hat{H}})^M, \]

where $\tau = \beta / M$. The factorized form of the density matrix facilitates Monte Carlo simulation because it allows for the calculation of the partition function using a series of imaginary time steps.
where \( \tau = \beta / M \) is the “time step” (by analogy to real-time path integrals in quantum mechanics). As \( M \to \infty \), \( \tau \to 0 \), and \( \rho_{1/M} = e^{-\tau \hat{H}} \) approaches the density matrix at infinite temperature (zero \( \beta \)).

In this limit, the high temperature density matrix can be approximated. Writing the Hamiltonian as a sum of kinetic and potential operator terms, \( \hat{\mathcal{H}} = \hat{T} + \hat{V} \), and applying an operator identity

\[
e^{-\tau (\hat{T} + \hat{V})} = e^{-\tau T} e^{-\tau V},
\]

we find that when \( \tau \) is small, we can ignore the quadratic commutator term and obtain the following “primitive approximation”,

\[
e^{-\tau \hat{\mathcal{H}}} \approx e^{-\tau \hat{T}} e^{-\tau \hat{V}},
\]

which factorizes the high-temperature density matrix into a product of exponentials. The neglect of the commutator \([\hat{T}, \hat{V}]\) in this approximation is justified by the Trotter formula \([178]\),

\[
e^{-\beta (\hat{T} + \hat{V})} = \lim_{M \to \infty} \left( e^{-\tau \hat{T}} e^{-\tau \hat{V}} \right)^M,
\]

which assures us that the density matrix is recovered when the number of \( M \) of time slices is large.

Inserting the primitive approximation into the path integral, Eq. B.11, results in considerable simplification; the kinetic portion can be integrated out exactly. This is the basis for the simplest form of path integral Monte Carlo. It is not very efficient, however; practical PIMC codes use improved approximations such as the pair-product action \([179, 180, 127]\), which approximates the potential as a sum of pair potentials. The sum becomes a product upon exponentiating (thus “pair product”), each factor of which can be evaluated exactly.

A PIMC simulation must propose two kinds of moves: path moves which alter the path of a particle, and permutation moves which permute the paths of several particles. For efficient simulation \([127]\), it is necessary to make multislice path moves (perturbing more than one time slice at a time) and to propose joint path and permutation moves. Perturbations of single slices are most efficient when performed according to the “heat bath” transition rule, in which a particle’s proposed position at a fixed time slice is sampled from a Gaussian distribution centered on its current position, of width proportional to \( \lambda_0 \tau \), where \( \lambda_0 \) is the zero point thermal wavelength (App. A.1).

Because permutations of the paths of \( N \) particles grow like \( N! \), permutation sampling is exponentially slow with increasing particle number. This has been a major limitation of the PIMC method in cases where quantum statistical exchange

---

\(^9\)Assuming the operators involved are self-adjoint and bounded below.
is important, such as in superfluid helium. Recently, however, the PIMC method has been extended to the grand canonical ensemble, allowing for the creation and destruction of particle paths [181, 182]. An effect of this extension, based on the “worm quantum Monte Carlo” lattice algorithm [183, 184], is to substantially overcome the permutation sampling barrier, allowing for simulated system sizes several orders of magnitude larger than earlier PIMC implementations.
Interaction potentials

C.1 Particle/particle

The Lennard-Jones (LJ) “12-6” semiempirical intermolecular potential [2] is among the most commonly used potentials in physisorption studies, due to its simplicity and adequate similarity to true intermolecular potentials. (See Sec. 1.1.1 for additional introductory discussion of physisorption potentials.) Depending only on the interparticle separation $r$, it is given by

$$V_{LJ}(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right],$$

where $\epsilon$ and $\sigma$ are parameters characterizing the potential well depth and equilibrium separation, respectively. The $r^{-12}$ term dictates the short-range repulsive behavior of the interaction, while the $-r^{-6}$ term dictates the long-range attractive behavior. (As noted in Sec. 1.1.1, the behavior is actually $r^{-7}$ at very long ranges that with which we are typically not concerned in condensed phases of matter.) The LJ potential is plotted in Figure C.1.

The potential well depth is interpreted as the binding energy between the particles.$^1$ It should be noted that while $\epsilon$ gives the exact well depth, $\sigma$ is only approximately the equilibrium interparticle separation; the actual separation is given by the minimum of the potential, $r_{\text{min}} = 2^{1/6}\sigma \approx 1.122\sigma$, or $\sigma \approx 0.891\, r_{\text{min}}$.

C.2 Particle/planar sheet

When an isolated particle interacts with an infinitesimally thin planar surface, or sheet, via the Lennard-Jones 12-6 interaction, the particle-substrate interaction

---

$^1$This is only true for classical particles. The quantum binding energy will be smaller due to the addition of zero point energy; the binding energy is controlled by the de Boer quantum parameter, which if sufficiently large can forbid the existence of bound states altogether [167].
potential is given by a pairwise sum of the Lennard-Jones interparticle potential between the isolated particle and each particle in the surface,

\[ V_{\text{sheet}}(x, y, z) = \Theta \int_{-\infty}^{\infty} dx' \int_{-\infty}^{\infty} dy' \int_{-\infty}^{\infty} dz' \frac{1}{r} V_{\text{LJ}}(r), \]

where \( \Theta \) is the 2D number density of particles in the substrate. This integral yields a 10^{-4} potential, depending only on \( z \),

\[ V_{\text{sheet}}(z) = \frac{2\pi}{5} \epsilon \Theta \sigma^2 \left[ 2 \left( \frac{\sigma}{r} \right)^{10} - 5 \left( \frac{\sigma}{r} \right)^4 \right]. \]

The particle-sheet equilibrium separation is given by the minimum of this potential, \( r_{\text{min}} = \sigma \). Its well depth is \( (6\pi/5)\Theta\sigma^2\epsilon \approx 3.77\Theta\sigma^2\epsilon \).

### C.3 Particle/planar bulk solid

Instead of an infinitesimally thin sheet (the plane \( z = 0 \)), we can consider a bulk solid with a planar surface (the half space \( z < 0 \)):

\[ V_{\text{planar solid}}(x, y, z) = \rho \int_{-\infty}^{\infty} dx' \int_{-\infty}^{\infty} dy' \int_{-\infty}^{0} dz' V_{\text{LJ}}(r), \]

where \( r = \sqrt{(x-x')^2 + (y-y')^2 + (z-z')^2} \),
where \( \rho \) is the 3D number density of particles in the substrate. Then the particle-solid interaction is given by a 9-3 interaction,

\[
V_{\text{planar solid}}(z) = \frac{2\pi}{45} \epsilon \rho \sigma^3 \left[ 2 \left( \frac{\sigma}{r} \right)^9 - 15 \left( \frac{\sigma}{r} \right)^3 \right]. \tag{C.5}
\]

The particle-solid equilibrium separation distance is given by the minimum of this potential, \( r_{\text{min}} = (2/5)^{1/6} \sigma \approx 0.858 \sigma \). Its well depth is \( \sqrt{40/81} \pi \rho \sigma^3 \epsilon \approx 2.208 \rho \sigma^3 \epsilon \).

It is often customary to express this 9-3 potential in terms of new parameters \( D \) and \( C_3 \), where \( D \) is the well depth and \( C_3 \) is the coefficient in front of the \(-z^{-3}\) term. Then

\[
V_{\text{planar solid}}(z) = \frac{4C_3^3}{27D^2z^3} - \frac{C_3}{z^3}, \tag{C.6}
\]

where \( D = \sqrt{40/81} \pi \rho \sigma^3 \epsilon \), \( C_3 = (2\pi/3)\epsilon \rho \sigma^6 \). In terms of these parameters, the equilibrium particle-surface separation is \( r_{\text{min}} = [2C_3/(3D)]^{1/3} \approx 0.874 (C_3/D)^{1/3} \).

The LJ 12-6 particle-particle parameters can be inferred from them as well, giving \( \sigma = \sqrt{10} C_3/(3D) \approx 1.018 (C_3/D)^{1/3}, \epsilon = 27D^2/(20\pi \rho C_3) \approx 0.430 D^2/(\rho C_3) \).

### C.4 Particle/cylindrical sheet

We next consider the case of substrate which is an infinitesimally thin sheet rolled up into a cylinder of radius \( R \): a tube. Then

\[
V_{\text{tube}}(x, y, z) = \Theta \int_{-\infty}^{\infty} dz' \int_0^{2\pi} R d\theta' V_{\text{LJ}}(r),
\]

\[
r = |r - r'|.
\]

After some simplification and changes of variables, this reduces to, in cylindrical coordinates,

\[
V_{\text{tube}}(r) = R\Theta \int_{-\infty}^{\infty} dz \int_0^{2\pi} d\theta V_{\text{LJ}}(\delta),
\]

\[
\delta = \sqrt{R^2 + r^2 - 2Rr \cos \theta} + z^2.
\]

Upon integration, this yields\(^2\)

\[
V_{\text{tube}}(r) = 3\pi \epsilon \theta \sigma^2 \left[ \frac{21}{32} \left( \frac{\sigma}{R} \right)^{10} M_{11} \left( \frac{r}{R} \right) - \left( \frac{\sigma}{R} \right)^4 M_5 \left( \frac{r}{R} \right) \right], \tag{C.9}
\]

where

\[
M_n(x) = \int_0^\pi d\theta (1 + x^2 - 2x \cos \theta)^{-n/2} = \frac{\pi}{2} (1 + x)^{-2n} 2F_1 \left( \frac{1}{2}, n; 1; \frac{4x}{(1 + x)^2} \right), \tag{C.10}
\]

\(^2\)This expression is also found in Eq. 2 of [149].
and \( _2F_1(a, b; c; z) \) is a hypergeometric function.

The particle-tube interaction potential found here is too complicated to admit analytic solutions for the well depth and equilibrium separation, but some series approximations are possible [149]; one starting point is the small-\( r \) Taylor expansion near the axis of the cylinder.

### C.5 Comparison of potential minima

In previous sections we found expressions for the equilibrium separation and binding energy in the cases of a particle interacting with another particle, with a planar sheet, and with a planar bulk solid. These parameters, characterizing the location and magnitude of the interaction potential minimum, were expressed in terms of the Lennard-Jones 12-6 particle-particle parameters \( \sigma \) and \( \epsilon \). It is useful to compare the values found in these cases; for instance, does a particle bind more or less strongly to, and closer or farther from, another particle than it would to a planar sheet made out of the same substance?

These comparisons are summarized in Tables C.1 and C.2. For instance, Table C.1 indicates that a particle of species \( X \) will bind to a planar sheet comprised of particle species \( Y \) at 0.891 times the distance it would bind to an isolated particle of species \( Y \); Table C.2 indicates that it will bind more strongly to the sheet if its density \( \Theta \gtrsim\ 0.265/\sigma^2 \).

An alternate formulation of Table C.2 would express the energy ratios purely in terms of parameters relevant to the systems being compared. For instance, the energy ratio for a particle interacting with a bulk solid compared to a sheet, \((\sqrt{250}/27)\rho\sigma/\Theta\), is currently expressed in terms of \( \sigma \). However, \( \sigma \) is a parameter related to a particle interacting with another particle, not with a surface. Instead, the ratio could be expressed as \((25/27)\rho r_s^3/\Theta\rho_s\), where \( r_s = \sigma \) is the equilibrium separation for a particle-sheet system and \( r_b = (2/5)^{1/6}\sigma \) is the equilibrium separation for a particle-bulk solid system. In this way, dependence upon parameters describing the irrelevant particle-particle binding energy can be eliminated when comparing particle-surface adsorption energies.
Table C.1. Comparison of the equilibrium particle/particle or particle/surface separations for three systems, given by the ratio of the separation for the system in row $i$ to the separation for the system in row $j$. The systems “particle”, “planar sheet”, and “planar bulk” refer to an isolated particle interacting with another isolated particle, with a planar sheet of particles, or with a planar solid bulk of particles, respectively.

<table>
<thead>
<tr>
<th></th>
<th>particle</th>
<th>planar sheet</th>
<th>planar bulk</th>
</tr>
</thead>
<tbody>
<tr>
<td>particle</td>
<td>1</td>
<td>$2^{1/6} \approx 1.122$</td>
<td>$5^{1/6} \approx 1.308$</td>
</tr>
<tr>
<td>planar sheet</td>
<td>$2^{-1/6} \approx 0.891$</td>
<td>1</td>
<td>$(2/5)^{-1/6} \approx 1.165$</td>
</tr>
<tr>
<td>planar bulk</td>
<td>$5^{-1/6} \approx 0.765$</td>
<td>$(2/5)^{1/6} \approx 0.858$</td>
<td>1</td>
</tr>
</tbody>
</table>

Table C.2. Comparison of the particle/particle or particle/surface binding energies for three systems, given by the ratio of the energy for the system in row $i$ to the energy for the system in row $j$. The systems “particle”, “planar sheet”, and “planar bulk” refer to an isolated particle interacting with another isolated particle, with a planar sheet of particles, or with a planar solid bulk of particles, respectively.

<table>
<thead>
<tr>
<th></th>
<th>particle</th>
<th>planar sheet</th>
<th>planar bulk</th>
</tr>
</thead>
<tbody>
<tr>
<td>particle</td>
<td>1</td>
<td>$5/(6\pi\Theta\sigma^2)$</td>
<td>$9/(\sqrt{40\pi})/(\rho\sigma^3)$</td>
</tr>
<tr>
<td></td>
<td>$\approx 0.265/(\Theta\sigma^2)$</td>
<td>$\approx 0.453/(\rho\sigma^3)$</td>
<td></td>
</tr>
<tr>
<td>planar sheet</td>
<td>$(6/5)\pi\Theta\sigma^2$</td>
<td>1</td>
<td>$(27/\sqrt{250})\Theta/(\rho\sigma)$</td>
</tr>
<tr>
<td></td>
<td>$\approx 3.77\Theta\sigma^2$</td>
<td></td>
<td>$\approx 1.708\Theta/(\rho\sigma)$</td>
</tr>
<tr>
<td>planar bulk</td>
<td>$(\sqrt{40\pi}/9)\rho\sigma^3$</td>
<td>$(\sqrt{250}/27)\rho\sigma/\Theta$</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>$\approx 2.208\rho\sigma^3$</td>
<td>$\approx 0.586\rho\sigma/\Theta$</td>
<td></td>
</tr>
</tbody>
</table>
Bibliography


Vita

Nathan Mark Urban

Nathan Mark Urban in 1997 earned B.S. degrees (cum laude) in Physics, Computer Science, and Mathematics from Virginia Tech (Blacksburg, VA). After two years employed as a software developer at InSystems Technologies, Inc. (Roanoke, VA), in 1999 he enrolled in the Ph.D. program in physics at the Pennsylvania State University (State College, PA). Since that time, he has been employed as a Research and Teaching Assistant in the Penn State physics department.

Prior to his thesis research, Nathan conducted research in the dynamical triangulation and spin foam approaches to quantum gravity, black hole quasinormal modes and gravitational wave astrophysics, loop quantum inflationary cosmology, Bayesian experimental data analysis, and the statistical properties of complex networks.

Nathan has also been actively involved in education. In 1996–1997 he was a high school student mentor at Virginia Tech, and there in 1997 he conceived, designed, and instructed an upper-level undergraduate course in general relativity. At Penn State, he taught recitations and laboratories for all of the introductory calculus-based physics courses. In 2005–2006 he assisted in the curriculum design of a new joint Physics/Science Education course, “Sound and Light”—a class in waves, acoustics, and optics for pre-service elementary education majors, in an experiential, student centered, evidence-based laboratory format—and served as volunteer teaching assistant and guest lecturer for the course. Concurrently with his Ph.D. he earned an M.Ed. in physics (higher education), in the field of active and constructivist learning in the college physics curriculum.

Nathan was awarded the 1993 “Investment in Excellence” Entering Freshman Scholarship from the Department of Computer Science at Virginia Tech, the 1997 Lubna Ijaz Scholarship for Physics and Service from the Department of Physics at Virginia Tech, and the 2005 David C. Duncan Graduate Fellowship from the Department of Physics at Penn State. He is a member of the American Physical Society (APS), the American Association of Physics Teachers (AAPT), the American Statistical Association (ASA), the Society for Industrial and Applied Mathematics (SIAM), and the Consortium for Mathematics and Its Applications (COMAP).