Atoms in nanotubes: small dimensions and variable dimensionality

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Newly discovered carbon nanotubes provide an environment in which small atoms move relatively freely. An assembly of such atoms provides a realization of a quasi-one dimensional system which is an ideal testing ground for concepts and mathematics of statistical physics.

I. INTRODUCTION

One of the recurrent themes in statistical physics is the sensitivity of natural phenomena to the spatial dimensionality of the system. The properties of three-dimensional (3D) matter (for example, solid argon) differ quantitatively from 2D matter made of the same constituent particles (for example, a layer of argon, one atom thick, deposited on a graphite surface). What may not be obvious is that the behavior of 3D systems is qualitatively different from that of 2D systems. For example, a monolayer film has properties which are sensitive to the underlying solid, such as its lattice constant. This film may exhibit ordered phases which have no 3D counterpart, such as commensurate solids. The collective modes of the system (for example, phonons) also will produce thermodynamic properties which depend on the dimensionality. More subtle are differences in the values of critical exponents which characterize thermodynamic singularities near phase transitions. These differences reflect the fact that the correlations responsible for order are more sensitive to fluctuations in 2D than in 3D. This sensitivity is even more dramatic in 1D systems and one consequence of these fluctuations is that no ordered phases may exist in 1D at finite temperature $T$.

One might wonder whether 1D systems exist in nature which can test this intriguing “null” hypothesis. This search has led us to explore the statistical mechanics of atoms moving in carbon nanotubes (see Fig. 1). We have found a remarkable variety of phenomena which exhibit a range of effective dimensionalities, depending on the thermodynamic variables (number of atoms $N$ and temperature $T$), microscopic variables (atomic size relative to nanotube radius), and the geometry (isolated tubes or ordered arrays of tubes). This paper discusses some aspects of the behavior that we have found, revealing the system to be a marvelous playground for concepts of thermal physics.

The field of carbon nanotubes was born in 1991 with the discovery by Iijima and the determination of conditions for the synthesis of large quantities of nanotubes. The tubes
consist of graphite sheets rolled up into hollow cylinders, and they appear as either single 
or coaxial cylinders, called single-wall and multi-wall nanotubes, respectively (see Fig. 1).
A remarkable feature is their width-to-length ratio, due to their very small diameters (∼ 14 Å) 
and relatively long lengths (on the order of tens of µm). Recent experiments have successfully 
produced bundles of single-wall nanotubes arranged in triangular lattices with a lattice constant of 17 Å. 
The distribution of radii of the tubes is narrowly peaked around 7 Å. This size is such that many species of small atoms (diameter of order 3 Å) fit comfortably within the tube and are therefore strongly imbibed by these tubes. In the 
nanotube bundle geometry we expect that small atoms are even more strongly adsorbed in 
the narrow interstitial channels between the tubes than within them. Indeed, a recent 
measurement for ⁴He found an interstitial binding energy which is 2.3 times as large as the 
binding energy on the basal plane of graphite (which is the highest for any planar surface).

The outline of the paper is the following. Sections II and III discuss the properties of 
weakly interacting quantum gases confined within these tubes. We find that the thermal 
behavior as a function of T and N corresponds to dimensions \( D = 1, 2, \) or \( 3 \). Section IV 
discusses the results of a numerical study of a strongly interacting fluid (helium), which 
exhibits extraordinary quasi-1D behavior (with a transition) when confined interstitially 
within a bundle of nanotubes. Section V discusses a dimensional crossover manifested by 
the phonons of a high density film adsorbed within a tube. Section VI summarizes these 
phenomena. This variety of behavior provides intriguing manifestations of novel physics and 
stimulating examples of the beauty present in the diverse field of statistical physics.

II. ULTRALOW DENSITY GAS

One of the simplest models in statistical physics is the classical ideal gas. May such 
a simple model be applied to atoms moving within the extremely anisotropic, confined 
geometry of a nanotube? The answer is yes, and the domain of classical ideal gas behavior 
is quite extended. The problem is interesting because it involves the quantum-mechanical 
spectrum of the individual particles, even though classical statistics describes the thermal 
properties of the gas as a whole. A surprising fact is that at any nonzero temperature there 
exists a density regime in which the classical ideal gas approximation is valid.

The classical ideal gas assumption implies that the probability that a single particle has 
energy \( E \) is proportional to the Boltzmann function, \( p(E) = e^{-\beta E} \), where \( \beta^{-1} = k_BT \). The 
mean energy \( U \) of the system of \( N \) atoms can be found from \( n(E) \), the density of states, 
and the average energy per particle \( \langle E \rangle = U/N \) is given by

\[
\langle E \rangle = \frac{\int dE E n(E) p(E)}{\int dE n(E) p(E)}.
\]

The behavior of this system resides in the function \( n(E) \), which we now consider for gases 
inside nanotubes.

An adequate approximation of the energy spectrum can be found by assuming that the 
atom’s potential energy is a function only of the radial coordinate \( r \). Then the Schrödinger 
equation is separable, and the resulting wave functions may be written as

\[
\Psi(r) = L^{-1/2} e^{ikz} \psi_{nv}(r, \varphi),
\]

where \( E = \hbar^2 k^2/2m + \epsilon_{nv} \), \( \epsilon_{nv} \) is the energy of transverse motion, \( L \) is the tube length, \( \varphi \) is the 
azimuthal angle, and \( k \) is the axial wave vector. Figure displays a model calculation of the
radial dependence of the potential energy of a He atom inside a nanotube of radius 5 Å. Also shown are the lowest lying eigenfunctions for motion in the plane perpendicular to the axis (the determination of the eigenfunctions is discussed in the Appendix). These eigenfunctions involve azimuthal excitation and are labelled by a quantum number \( \nu \), corresponding to wave functions

\[
\psi_{1\nu}(r, \varphi) = f_{1\nu}(r)e^{i\nu \varphi},
\]

where \( \nu \) is an integer, and \( f_{1\nu}(r) \) is the radial wave function. Because of the small tube size, the radial degree of freedom has a large excitation energy. Hence, at low temperature we may neglect the thermal contribution from all radially excited states and consider only states with \( n = 1 \). Under these circumstances, the effective dimensionality is two, arising from the azimuthal and longitudinal excitations, respectively. Intriguing behavior arises when we address the axial motion. The density of states for 1D motion alone is

\[
n_{\text{axial}}(E) = b E^{-1/2}, \quad b = \left(\frac{g L}{\hbar}\right) \left(\frac{2m}{1}\right)^{1/2},
\]

where \( g \) is the spin degeneracy. Together with the azimuthal excitation, we now have two “active” degrees of freedom. The total density of states is

\[
n(E) = \sum_{\nu} b (E - \epsilon_{1\nu})^{-1/2} H(E - \epsilon_{1\nu}),
\]

where \( H \) is the Heaviside step function and the sum is over \( \nu = 0, \pm 1, \pm 2, \ldots \). The states with \( \nu \neq 0 \) are doubly degenerate, while the \( \nu = 0 \) state is nondegenerate. Figure 3 shows \( n(E) \), which has a serrated shape due to the onset of successive azimuthal contributions. At very low \( T \), only the 1D motion, corresponding to \( \nu = 0 \), is excited, while higher \( \nu \) values become relevant at higher \( T \). Figure 4 shows the dimensionless specific heat \( c \equiv C/Nk_B \) calculated from this spectrum for a system of \( N \) particles. Note that the low \( T \) behavior exhibits a specific heat equal to the 1D classical ideal gas value \( (c = 1/2) \), while the high \( T \) limit is the 2D value \( (c = 1) \). The overshoot behavior in the intermediate crossover region of \( T \) in Fig. 4 \((c > 1)\) is reminiscent of that seen in the specific heat of diatomic molecules which is expected because of a qualitatively similar excitation spectrum. The dimensionality crossover occurs at a value of \( T \) corresponding approximately to the first azimuthal excitation energy. As seen in Fig. 4, this value of \( T \) depends on the nanotube radius \( R \), as a greater \( R \) implies smaller azimuthal energy. Figure 5 shows how the effective dimensionality crossover depends on \( R \) and \( T \) for helium. The effective dimensionality variation (from one to three as \( T \) is increased) is a general feature of the system.

We now address the issue of the validity of the classical ideal gas approximation. At sufficiently high \( T \), quantum corrections can be evaluated from a virial (Wigner-Kirkwood) expansion, as is familiar from statistical physics. Quantum statistical corrections become important when the de Broglie thermal wave length \( \lambda_T = (2\pi \beta \hbar^2/m)^{1/2} \) becomes comparable to the interparticle spacing \( (L/N) \) along the tube. More interesting perhaps is the effects of interactions. There are two heuristic arguments which imply that (even at very low \( T \)) there will always exist a density below which the classical ideal limiting behavior occurs. One is simply that the quasi-1D system does not condense (at finite \( T \)). This behavior is nearly unique; to our knowledge, analogous (equilibrium) behavior for neutral particles
exists only for spin polarized atomic hydrogen. The second argument pertains to the effect of the “hard-core” repulsion between atoms. We will show elsewhere that the spread of the single particle wave functions around the perimeter of the tube is sufficient to reduce the core effect, that is, allow atoms to pass by one another.

III. FINITE DENSITY IDEAL QUANTUM GAS

At a finite density we need to evaluate the effect of quantum statistics even if the gas is noninteracting, because at low $T$ the system becomes degenerate. The calculational procedure is a straightforward extension of that conventionally used for 3D translationally invariant systems. We must determine the energy of the system

$$ U = \int dE E n(E) f_\pm(E) $$

where $f_\pm(E)$ is the Bose or Fermi occupation function:

$$ f_\pm(E) = \frac{1}{e^{\beta(E-\mu)} \pm 1}. $$

The chemical potential $\mu$ is implicitly determined by the number of atoms:

$$ N = \int dE n(E) f_E(E). $$

We have performed this numerical procedure for Fermi systems having various numbers of particles $N$. Each value of $N$ yields a different Fermi energy determined by

$$ N = \int^{E_F} dE n(E). $$

For convenience, we shift the zero of energy to be $\epsilon_{10}$, the lowest azimuthal energy. For $R = 5 \AA$ and $^3$He, the first excited state, $\epsilon_{11}$, is at an energy $\Delta/k_B = 2.3$ K, as seen in Fig. 3. The three examples we will discuss have Fermi energies $E_F = 0.05, 0.95,$ and $1.05 \Delta$, respectively, as indicated in Fig. 3. These values were chosen to demonstrate the variety of crossover (classical/quantum and 1D/2D) behavior in this system.

At each density, the system remains classical down to a degeneracy temperature $T_d = E_F/k_B$. This behavior is most clearly seen in Fig. 3 for the low density ($E_F = 0.05 \Delta$) case, for which $T_d \sim 0.1$ K. For the two higher densities, the higher degeneracy temperature implies that the classical regime appears only at higher $T$, that is, above $T \sim 2$ K, as seen in Fig. 3. Above that value, the effect of the statistics is negligible, that is, the results of Section II apply (as in Fig. 3). As $T$ falls below $T_d$, quantum effects drive the specific heat to zero; the extreme degenerate behavior of a quantum system is given in terms of the density of states at the Fermi energy:

$$ C_V/k_B \simeq \frac{\pi^2}{3} n(E_F) k_B T. $$

In the degenerate regime of very low $T$, Eq. (10) applied to our three densities yields dramatically different slopes at low $T$, as is consistent with the infinite discontinuity in the density of states at the threshold for exciting the first azimuthal level (see Eq. 5) and
Fig. 3). Specifically, at $E_F = 1.05 \Delta$ the low $T$ specific heat is a factor of ten higher than at $E_F = 0.95 \Delta$, while it is approximately double that at $E_F = 0.05 \Delta$.

Note the curves in Fig. 6 at finite density have values of $C/Nk_B$ which are below the classical curve of Fig. 4. This behavior is a consequence of the fact that the quantum energy must coincide with the classical energy at high $T$. Hence the integrated heat capacity difference satisfies

$$\int_0^\infty dT (C - C_{\text{classical}}) = U_0,$$

where $U_0$ is the energy of the system at $T = 0$, corresponding to all states below the Fermi energy being fully occupied. At high $N$, the right side is very large, so the “quantum deficiency” $C - C_{\text{classical}}$ must be very large.

Qualitatively similar effects of quantum degeneracy occur for Bose systems. At high $T$, the system deviates from the classical ideal gas when $L/N$ becomes comparable to the de Broglie wave length, that is, when the delocalized single-particle wave functions overlap. We focus, instead, on the very low $T$ regime. Here one finds the following behavior by applying conventional low $T$ expansion techniques. The low-$T$ specific heat can be shown to satisfy

$$C/Nk_B = (3\zeta(3/2)/4)gL/N\lambda_T,$$

where $\zeta(x)$ is the Riemann zeta function. Equation (12) holds in the regime where the right-hand side is much less than one. Therefore, in this regime, the specific heat scales as $T^{d/2}$. It is amusing to find the general behavior of the specific heat of a Bose gas to be of the form $T^{d/2}$, even in the anomalous ($d > 2$) case of Bose-Einstein condensation. The expression for each dimensionality has essentially the same form, with the rightmost term raised to the power $d/2$.

At low $T$ the interactions between real particles usually cannot be neglected and the ideality assumption fails (except at very low density). Phonon-like collective modes appear in the Fermi and the Bose cases, while spin waves appear in the case of spin, corresponding to the realization of a so-called Luttinger liquid. To our knowledge, this concept has not yet been applied to the nanotube problem.

**IV. INTERACTING FLUIDS**

We now consider systems of interacting atoms confined to within nanotubes. In some cases, these may be adequately described by classical statistical mechanics, while in others cases a quantum treatment is necessary. The division between these cases is conventionally made by evaluating the De Boer quantum parameter $\Lambda^*$, which is a dimensionless measure of the ratio of quantum kinetic energy to potential energy:

$$\Lambda^* = h/\sigma(m\varepsilon)^{1/2}.$$  \hspace{1cm} (13)

Here $\sigma$ and $\varepsilon$ are parameters of the Lennard-Jones interaction between atoms of mass $m$:

$$V = 4\varepsilon[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}].$$  \hspace{1cm} (14)

When $\Lambda^*$ is “small,” classical theory is usually applicable, while otherwise quantum effects are not negligible. For example, argon ($\Lambda^* = 0.063$) and heavier inert gases are classical in
their behavior. The light and weakly interacting systems \( H_2 (\Lambda^* = 1.72) \) and \( ^4\text{He} (\Lambda^* = 3.2) \) are fully quantum mechanical, while neon \( (\Lambda^* = 0.58) \) is a borderline case of modest quantum corrections to the thermal properties.\textsuperscript{26}

Little theoretical work has been carried out so far for interacting atoms in single nanotubes. There is, however, a related situation for which some interesting results exist. That is the case of an ordered array of nanotubes, which form a close-packed bundle similar to strands of bucatini\textsuperscript{27} held tightly in one’s hand. We have found that tiny atoms are strongly attracted to the interstices between the tubes; these spaces are sufficiently small that a purely 1D theory may be applicable.\textsuperscript{7} This limit conveniently permits clean statistical mechanical calculations. For example, there is the venerable problem of the 1D classical gas of particles of specified hard core diameter \( a \), which was solved by Tonks and Langmuir.\textsuperscript{28} The 1D pressure satisfies

\[
p = k_B T/(L/N - a).
\]  

Interestingly, the classical system lends itself to an exact analytical treatment even in the case of more general interactions, as long as only nearest neighbors interact.\textsuperscript{29}

From a fundamental point of view, the most interesting case may be the extreme quantum case of He. Figure 7 shows the energy per atom of \(^4\text{He} \) in 1D at \( T = 0 \), computed with the Diffusion Monte Carlo (DMC) method.\textsuperscript{30} The data in the inset indicate that there may exist a low density bound state; that is, the 1D ground state is a liquid. This finding has been corroborated by a recent variational calculation of Krotscheck and Miller.\textsuperscript{31} The binding energy is very small, of the order of 10 mK per atom, at a mean interatomic spacing of about 15 \( \text{Å} \). Such a small cohesive energy is even less than what one might have expected from an extrapolation of the decrease in binding known to occur on reducing from 3D \( (E/N = -7.2K) \) to 2D \( (E/N = -0.8K) \) liquid He.\textsuperscript{32,33}

As indicated in Section I, there can be no phase transition in 1D at finite \( T \); this implies that the condensed state is absent except at \( T = 0 \). A fragile liquid can exist, however, at \( T \neq 0 \), in a nanotube bundle array, due to the cooperative attractive interactions from atoms in neighboring tubes. Such a novel anisotropic quantum fluid would be of immense fundamental interest. If one recalls\textsuperscript{34} that 2D Bose systems exhibit superfluidity without Bose condensation, one wonders what might be the properties of this quasi-1D fluid. No research has been done thus far to explore this question.

V. DIMENSIONALITY CROSSOVER OF THE PHONONS

The previous discussion pertains to the regime when the adsorbed material is a fluid. At high density, there are other interesting possibilities. One example involves a bundle of nanotubes (because it provides a 3D environment), which can permit the formation of solids within the tubes. Atoms of diameters \( \sim 3\text{Å} \) will form a cylindrical shell film coating the nanotube wall. If we turn to the thermal excitation of this solid, we encounter another instance of varying effective dimensionality. This is the case of phonon excitation. We have studied\textsuperscript{6} the specific heat arising from the phonons (assuming that the film’s atoms lie on a cylinder of radius \( R \) and possess an isotropic speed of sound \( s \)). The calculation evaluates the total energy

\[
U = \sum_{\alpha} \frac{\hbar \omega_{\alpha}}{e^{\beta \hbar \omega_{\alpha}} - 1}.
\]  

6
where $\omega_\alpha$ is the frequency of phonon mode $\alpha$ (which, in general, is characterized by axial and azimuthal contributions). The results are shown in Figs. 8 and 9. Figure 8 shows the relationship between a dimensionless function proportional to $C/T$

$$F(T) = (C/k_B)(\lambda/L),$$

and a dimensionless temperature

$$t = R/\lambda.$$  \hspace{1cm} (17)

Here

$$\lambda = h/\beta s$$  \hspace{1cm} (18)

is the thermal phonon wave length at temperature $T$. Note that the heat capacity is linear in $T$ at low temperature while the high temperature result is quadratic in $T$. This crossover is analogous to that found for the classical ideal gas: at low $T$ only phonons having wave vectors directed along the axis are excited, while at high $T$ the azimuthal modes also become excited. The effective dimensionality is seen in Fig. 8 to change from one to two when $R$ becomes about $0.15\lambda$. This value is where the circumference becomes nearly equal to a thermal wave length, which is a very logical onset condition for the azimuthal degree of freedom. Fig. 9 shows how the 1D and 2D regimes depend on the specific material; this behavior depends only on the value of $s$, which is a function of film density.

VI. CONCLUSIONS

From the preceding examples it is evident that atoms in nanotubes exhibit unusual properties which fascinate and stimulate our imagination. We have only briefly alluded to a subset of the wide variety of simple research problems which are yet to be thoroughly explored. Although many of these problems involve numerical methods, others are amenable to simple modelling. These should provide an inspiration to both students of statistical physics and researchers in condensed matter physics.

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APPENDIX. DETERMINATION OF THE WAVE FUNCTIONS

For a potential possessing cylindrical symmetry, the radial Schrödinger equation becomes

$$\frac{d^2f}{dr^2} + \frac{1}{r} \frac{df}{dr} + \left\{ \frac{2m}{\hbar^2} [\epsilon_{n\nu} - V(r)] - \frac{\nu^2}{r^2} \right\} f = 0,$$  \hspace{1cm} (20)

where $f(r)$ is the radial wave function. In general, solving Eq. 20 requires using a numerical method, for example the Numerov method. Instead, a simple way of estimating the energy levels $\epsilon_{n\nu}$ is to use a piecewise constant model potential constructed as shown in Fig. 2. Let $V(r) = V_0$ for $0 < r < a$, where $a$ is the inner distance at which the potential is $(V_{\min} + V_0)/2$.
$V_{\text{min}}$ is the minimum of the potential. We set $V(r) = V_{\text{min}}$ in the interval $a < r < b$, where $b$ is the zero-energy turning point of the carbon hard wall. Finally, we let $V = \infty$ for $r > b$.

For the case $\epsilon < V_0$ considered here, the radial wave function has the general form

$$f(r) = \begin{cases} A I_\nu(\kappa r) & \text{for } r < a, \\ B \left[ J_\nu(\chi r) - N_\nu(\chi r) \frac{J_\nu(\chi b)}{N_\nu(\chi b)} \right] & \text{for } a < r < b. \end{cases}$$

(21)

where $J_\nu, N_\nu$ are ordinary Bessel functions, and $I_\nu$ are modified Bessel functions. Here, $|\epsilon - V_0| = \hbar^2 \kappa^2 / 2m$, and $\epsilon + V_{\text{min}} = \hbar^2 \chi^2 / 2m$. Using the matching conditions, the eigenvalue problem reduces to the solution of the transcendental equation:

$$\frac{\kappa I'_\nu(\kappa a)}{I_\nu(\kappa a)} = \frac{\chi \left[ J'_\nu(\chi a) N_\nu(\chi b) - N'_\nu(\chi a) J_\nu(\chi b) \right]}{J_\nu(\chi a) N_\nu(\chi b) - N_\nu(\chi a) J_\nu(\chi b)},$$

(22)

where the prime refers to a derivative with respect to $r$. 

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FIGURES

FIG. 1. Scanning tunneling microscope picture of a single-wall nanotube, revealing the hexagonal atomic structure. The tube’s radius is 14 Å. Adapted from the original (color) version which appeared in Ref. [8].

FIG. 2. The model potential (—) and the true potential (— —) for $^3$He inside a single-wall nanotube with $R=5$ Å. The ground state energy (· · ·) and the first radially excited eigenstate (— · —), as well as the second excited azimuthal energy level (— —) are also represented (the first excited azimuthal energy level is indistinguishable from the ground state on this scale). The wave functions (unnormalized) shown correspond to the ground state (○), the first azimuthally excited state (✷) and the first radially excited state (+).

FIG. 3. The density of states (Eq. (5)) for $^3$He inside a single-wall tube of radius 5 Å (—) compared with the 2D density of states for $^3$He on a flat surface (— —). $n_{2D}$ is the density of states on a flat surface with the same area $\mathcal{A}$, $n_{2D} = m \mathcal{A} / (2 \pi \hbar^2)$. The arrows indicate the three Fermi energies considered.

FIG. 4. Crossover of specific heat from that of a 1D gas at low $T$ ($c=1/2$) to that of a 2D gas at high $T$ ($c=1$) in the case of $^3$He inside a single-wall nanotube of radius 5 Å (—) and 8 Å (— —).

FIG. 5. The 1D and 2D regimes for $^3$He inside a single wall nanotube. The solid line represents a characteristic azimuthal excitation temperature estimated by $T \simeq \hbar^2/[2mk_B(R')^2]$ (Ref. [4]), where $R'$ is the mean distance of the atom from the center of the tube. Actual azimuthal excitation energies (■) and radial excitation energies (♦, fitted by dotted line) for radii of 5 Å and 8 Å are shown. The temperature was expressed in Kelvin. The circle represents the experimental [35] vibrational excitation energy for $^3$He adsorbed on a flat surface of graphite.

FIG. 6. The specific heat as a function of $T$ for noninteracting $^3$He ($R=5$ Å) with densities $N_1$ (—), $N_2$ (— —), and $N_3$ (— · —), respectively, as defined in text, as well as the case of a purely 1D system (· · ·).

FIG. 7. The energy per particle of 1D $^4$He as a function of density at $T = 0$. The inset shows the low density regime. (Reproduced from Ref. [7]).

FIG. 8. The dimensionless ratio (defined in Eq. (18)) of the phonon heat capacity to the temperature (—), as a function of the dimensionless temperature $t$ (defined in Eq. (18)). The dotted curve displays the constant (linear) dependence on $T$ expected for $C/T$ in a 1D (2D) system. The actual plot reveals a crossover between 1D and 2D behavior in the nanotubes. (Reproduced from Ref. [6]).
FIG. 9. The relation between crossover temperature and the radius of the cylindrical shell containing the film. The curves correspond to different phases of He films and the case of a solid Xe film. The scaling temperature $T_R = \hbar s/(k_B R)$ is seen to depend on the specific material parameters. (Reproduced from Ref. [6]).
FIG. 2
FIG. 5
FIG. 6
FIG. 7
FIG. 8
FIG. 9