Atoms in nanotubes: Small dimensions and variable dimensionality

George Stan
Department of Physics and Center for Materials Physics, Pennsylvania State University, University Park, Pennsylvania 16802

Silvina M. Gatica
Department of Physics and Center for Materials Physics, Pennsylvania State University, University Park, Pennsylvania 16802 and Departamento de Física, Universidad de Buenos Aires, Buenos Aires 1428, Argentina

Massimo Boninsegni
Department of Physics, San Diego State University, San Diego, California 92182

Stefano Curtarolo and Milton W. Cole
Department of Physics and Center for Materials Physics, Pennsylvania State University, University Park, Pennsylvania 16802

(Received 10 February 1999; accepted 11 May 1999)

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 can be used to illustrate the concepts of statistical physics. © 1999 American Association of Physics Teachers.

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 type of particles (for example, a monolayer of argon deposited on a graphite surface). What might not be obvious is that the behavior of 3D systems is qualitatively different from 2D systems. For example, a monolayer film has properties which are sensitive to the underlying solid. The 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 yield thermodynamic properties which depend on the dimensionality. More subtle are differences in the values of critical exponents which characterize thermodynamic singularities near continuous phase transitions. These differences reflect the fact that correlations are more sensitive to fluctuations in 2D than in 3D. This sensitivity is even more dramatic in 1D systems; one consequence of these fluctuations is that no ordered phases may exist in 1D at finite temperature.

One might wonder whether 1D systems exist which can test this 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 wide range of effective dimensionalities depending on the thermodynamic variables (number of atoms and temperature), 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 the concepts of thermal physics.

Carbon nanotubes were discovered in 1991 and the conditions for the synthesis of large quantities were determined shortly thereafter. The tubes consist of graphite sheets rolled up into hollow cylinders, and they appear as either single or coaxial cylinders, called single-wall and multiwall 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. A recent measurement for 4He found an interstitial binding energy which is 2.3 times larger than the binding energy on the basal plane of graphite (which is the highest for any planar surface). The outline of the paper is as follows. Sections II and III discuss the properties of weakly interacting quantum gases confined in these tubes. We find that the thermal behavior as a function of density and temperature 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. The 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 application is interesting because it involves the quantum-mechanical spectrum of the individual particles, even though...
classical statistics describe the thermal properties of the gas as a whole. A surprising fact is that at any nonzero temperature $T$, there is a density regime in which the classical ideal gas approximation is valid.

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

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

(1)

The behavior of the system depends on $n(E)$, whose form we now consider for gases inside nanotubes.

An adequate approximation for $n(E)$ can be found by assuming that the atom’s potential energy is a function only of the radial coordinate $r$. In this case, Schrödinger’s equation is separable, and the resulting wave functions may be written as

$$\Psi(r) = L^{-1/2} e^{ikz} \psi_n(r),$$

(2)

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 2 displays a model calculation of the radial dependence of the potential energy of a He atom inside a nanotube of radius $5 \text{ Å}$. 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 low-lying eigenfunctions involve azimuthal excitation and are labeled by a quantum number $v$, corresponding to wave functions

$$\psi_{1,v}(r, \varphi) = f_{1,v}(r) e^{i v \varphi},$$

(3)

where $v$ is an integer, and $f_{1,v}(r)$ is the radial wave function. Because of the small tube size, the radial degree of freedom has a large excitation energy. Hence, at low temperatures 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 2, arising from the azimuthal and longitudinal excitations.

Intriguing behavior arises when we address the axial motion. The density of states for 1D motion alone is

$$n_{\text{axial}}(E) = b E^{-1/2}, \quad b = (g L / \hbar)(2m)^{1/2},$$

(4)

where $g$ is the spin degeneracy. Together with the azimuthal excitation, we have two “active” degrees of freedom, and the total density of states is

$$n(E) = \sum_{v=0, \pm 1, \pm 2, \ldots} b (E - \epsilon_{1,v})^{-1/2} H(E - \epsilon_{1,v}),$$

(5)

where $H$ is the Heaviside step function. The states with $v \neq 0$ are doubly degenerate, while the $v = 0$ 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 $v = 0$, is excited, while higher $v$ values become relevant at higher $T$. Figure 4 shows the dimensionless specific heat $c = C / N k_B$ 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 observed in the specific heat of diatomic molecules, which is expected because of a qualitatively similar excitation spectrum. The dimensionality crossover

![Image](https://via.placeholder.com/150)

![Image](https://via.placeholder.com/150)

![Image](https://via.placeholder.com/150)

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

Fig. 2. The model potential (—) and the true potential (---) for $^3$He inside a single-wall nanotube with $R = 5 \text{ Å}$. The ground-state energy (full curve) 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 (——). The quantity $n_{2D} = m A / (2 \pi \hbar^2)$ is the density of states on a flat surface with the same area $A$. The arrows indicate the three Fermi energies considered.
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 variation of the effective dimensionality (from 1 to 3 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. Quantum statistical corrections become important when the de Broglie thermal wave length $\lambda_T=(2\pi\hbar^2/m)^{1/2}$ becomes comparable to the interparticle spacing ($L/N)$ along the tube. More interesting perhaps is the effect of interactions. There are two heuristic arguments which imply that (even at very low $T$) there is always a density below which the ideal classical 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.\textsuperscript{19} The second argument pertains to the effect of the “hard-core” repulsion between atoms. We will show elsewhere\textsuperscript{20} 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 fixed 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 numerically by the number of atoms

$$N = \int dE \, n(E) f_\pm(E).$$

The internal energy can be computed numerically from Eq. (6). Each value of $N$ yields a different Fermi energy determined by

$$N = \int_{\epsilon_{10}}^{E_F} dE \, n(E).$$

For convenience, we shift the zero of energy to be $\epsilon_{10}$, the lowest azimuthal energy. For $R=5$ Å 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 are 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 $T_F=E_F/k_B$. This behavior is most clearly seen in Fig. 6 for the low density ($E_F=0.05 \Delta$) case, for which $T_F\approx 0.1K$. For the two higher densities, the higher degeneracy temperature implies that the classical regime appears above $T \approx 2K$, as seen in Fig. 6. Above this value, the effect of the statistics is negligible, that is, the results of Sec. II apply (as in Fig. 4). For $T<T_F$, quantum effects drive the specific heat to zero. The specific heat for $T\ll T_F$ is given in terms of the density of states at the Fermi energy\textsuperscript{21}

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

The application of Eq. (10) to our three densities yields dramatically different slopes at low $T$, 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]. Note that for $E_F=1.05 \Delta$, the low $T$ specific heat is a factor
of 10 higher than at $E_F=0.95\Delta$, while it is approximately double that at $E_F=0.05\Delta$.

Note the values of $C/Nk_B$ in Fig. 6 are below the classical curve of Fig. 4. This behavior is a consequence of the fact that the quantum-mechanical expression for the energy at low $T$ must coincide with the classical energy at high $T$. Hence, the integrated heat capacity difference satisfies

$$\int_0^\infty dT (C - C_{\text{classical}}) = U_0,$$  \hspace{1cm} (11)

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.

Similar quantum degeneracy effects 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 on the very low $T$ regime. The low-$T$ specific heat can be shown to satisfy \(^{22}\)

$$C/Nk_B = (3g \zeta(3/2) / 4) L / (N\lambda_T),$$ \hspace{1cm} (12)

where $\zeta(x)$ is the Riemann zeta function. Equation (12) holds when the right-hand side is much less than 1. In this regime, the specific heat scales as $T^{1/2}$. It is amusing that the general behavior of the specific heat of a Bose gas has the form $T^{d/2}$, even in the anomalous ($d>2$) case of Bose–Einstein condensation. \(^{23}\)

At low $T$, the interparticle interactions cannot be neglected and the ideal gas assumption fails (except at very low density). Phonon-like collective modes appear in the Fermi and the Bose cases, \(^{24}\) while spin waves appear if the particles have spin, corresponding to the realization of a so-called Luttinger liquid. \(^{25}\) 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 nanotubes. These systems may be adequately described by classical or quantum statistical mechanics depending on the value of the De Boer quantum parameter $\Lambda^*$, a dimensionless measure of the ratio of quantum kinetic energy to potential energy. \(^{26}\)

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

Here, $\sigma$ and $e$ are parameters of the Lennard-Jones interaction between atoms of mass $m$.

$$V = 4e [ (\sigma / r)^{12} - (\sigma / r)^{6}].$$ \hspace{1cm} (14)

When $\Lambda^*$ is "small," classical theory is applicable; otherwise, quantum effects are not negligible. For example, argon ($\Lambda^*=0.063$) and the heavier inert gases are classical in their behavior, the light and weakly interacting systems $H_2$ ($\Lambda^*=1.72$) and $^4$He ($\Lambda^*=3.2$) are fully quantum mechanical, and neon ($\Lambda^*=0.58$) is a borderline case of modest quantum corrections to its thermal properties. \(^{27}\)

Little theoretical work has been done so far for interacting atoms in single nanotubes. However, some interesting results exist for an ordered array of nanotubes which forms a close-packed bundle similar to strands of bucatini \(^{28}\) held tightly in one's hand. Tiny atoms are strongly attracted to the interstices between the tubes; these spaces are sufficiently small that a purely 1D theory may be applicable. \(^{27}\) This limit conveniently permits statistical mechanical calculations. For example, there is the venerable problem of the 1D classical gas of particles of hard-core diameter $a$, which was solved exactly by Tonks and Langmuir. \(^{29}\) The 1D pressure satisfies $p = k_B T / (L/N - a)$. The classical system lends itself to an exact analytical treatment even for more general interactions, as long as only nearest neighbors interact. \(^{30}\)

The most interesting case might be the extreme quantum case of He. Figure 7 shows the energy per atom of $^4$He in 1D at $T=0$, computed with the diffusion Monte Carlo (DMC) method. \(^{31}\) The data in the inset indicate that a low-density bound state might exist; that is, the 1D ground state is a liquid. This observation has been corroborated by a recent variational calculation and by a new DMC calculation. \(^{32}\) The binding energy is very small, of the order of 2 mK per atom, at a mean interatomic spacing of about 15 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 ($E/N = -7.2$ K) to 2D ($E/N = -0.8$ K) liquid He. \(^{33,34}\)

As indicated in Sec. I, there is no phase transition in 1D at finite $T$, which implies that the condensed state is absent except at $T=0$. A weakly bound liquid can exist, however, at $T\neq0$, in a nanotube bundle array due to the cooperative at-

![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.)](image-url)
tractive interactions from atoms in neighboring tubes. Such a novel anisotropic quantum fluid would be of immense fundamental interest. If we recall that 2D Bose systems exhibit superfluidity without Bose condensation, what would be the properties of this quasi-1D fluid? No research has been done so 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 diameter ~3 Å will form a cylindrical shell film coating the nanotube wall. If we consider the thermal excitation of this solid, we encounter another instance of varying effective dimensionality. We have studied the specific heat arising from this quasi-1D solid, we encounter another instance of varying effective dimensionality. We have studied the specific heat arising from this quasi-1D solid, which is a function of film density. The actual plot reveals a crossover from 1D to 2D behavior in the nanotubes. (Reproduced from Ref. 6.)

The results are shown in Figs. 8 and 9. Figure 8 shows the dimensionless ratio of the phonon heat capacity to the temperature (—), as a function of the dimensionless temperature $t = T/T_R = R/\lambda$. 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.)

VI. SUMMARY

From the preceding examples it is evident that atoms in nanotubes exhibit unusual properties which fascinate and stimulate our imagination. We have only briefly discussed 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 a simple qualitative understanding. These problems should provide an inspiration to both students of statistical physics and researchers in condensed matter physics.


ACKNOWLEDGMENTS

We would like to thank Aldo Migone, Moses Chan, Jainendra Jain, Yong-Baek Kim, Karl Johnson, A. T. Johnson, Ana Maria Vidales, and Vincent Crespi for very useful discussions. We are happy to acknowledge support from the National Science Foundation under Research Grant Nos. DMR-9705270 and DMR-9802803 and ACS-PRF #31641-AC5 from the Petroleum Research Fund of the American Chemical Society.

APPENDIX: DETERMINATION OF THE WAVE FUNCTIONS

For a potential possessing cylindrical symmetry, the radial Schrödinger equation becomes
where the prime refers to a derivative with respect to \( r \).

where

\[ V(r) = V_0 \]

for \( 0 < r < a \), where \( a \) is the inner distance at which the potential is \((V_{\text{min}} + V_0)/2\); \( V_{\text{min}} \) 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 \( \epsilon < V_0 \), the radial wave function has the general form

\[
 f(r) = \begin{cases} 
  A J_\nu(kr) & \text{for } r < a, \\
  B \left[ J_\nu(xr) - N_\nu(xr) J_\nu(yb) \right] / N_\nu(yb), & \text{for } a < r < b,
\end{cases}
\]

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

\[
 \frac{\kappa_\nu'(ka)}{\kappa_\nu'(ka)} = \frac{\chi[J_\nu(xa)N_\nu(yb) - N_\nu(xa)J_\nu(yb)]}{J_\nu(xa)N_\nu(yb) - N_\nu(xa)J_\nu(yb)},
\]

where the prime refers to a derivative with respect to \( r \).

\[ A \text{ and } B \text{ are determined by the boundary conditions at } r = a \text{ and } r = b. \]


16 In 1D, the number of states in an interval \([k, k + dk] \) is \((L/2\pi)dk\), corresponding to an energy interval \( d\epsilon = \hbar^2 k^2 / 2m \). Taking into account degenerate states of negative energy vector \( k \), the density of states (number per unit energy) is \( mL/(2\pi\hbar^2) \), which yields Eq. (4).

17 For see, Fig. 6.5 in R. K. Pathria, Statistical Mechanics (Butterworth Heinemann, Oxford, 1996), pp. 146.

18 The excitation spectrum for the linear rotator (for example, the rigid diatomic molecule) has a similar form \((\epsilon = 1(1+\epsilon))\) and exhibits an over-shoot of the heat capacity above \( C/Nk_B = 1 \).


23 For see, Fig. 6.5 in R. K. Pathria, Statistical Mechanics (Butterworth Heinemann, Oxford, 1996), pp. 146.

24 The excitation spectrum for the linear rotator (for example, the rigid diatomic molecule) has a similar form \((\epsilon = 1(1+\epsilon))\) and exhibits an over-shoot of the heat capacity above \( C/Nk_B = 1 \).


28 The derivation of this result follows closely the corresponding 3D one described in R. K. Pathria, in Ref. 17, Eq. (31), Chap. 7.


32 The quantum kinetic energy per particle due to a particle’s confinement by its neighbors at distance \( \sigma \) is order \( \hbar^2 / (4m\sigma^2) \), while the potential energy is order \( \epsilon \).


34 Bucatini is a pasta that has a hole along the axis of each strand.
33 If the Lennard-Jones 6-12 model (with parameters $\epsilon=10.22$ K and $\sigma=2.56$ Å) were an accurate description of the He–He interaction $V(r)$, He would form a 1D condensed ground state (L. W. Bruch, private communication, 1998).

OPTIMUM INTELLIGENCE

To be highly successful the scientist must be confident enough to steer for blue water, abandoning sight of land for a while. He values risk for its own sake. He keeps in mind that the footnotes of forgotten treatises are strewn with the names of the gifted but timid. If on the other hand he chooses like the vast majority of his colleagues to hug the coast, he must be fortunate enough to possess what I like to define as optimum intelligence for normal science: bright enough to see what needs to be done but not so bright as to suffer boredom doing it.