Universal anisotropic condensation transition of gases in nanotube bundles

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Abstract

Gases adsorbed within bundles of carbon nanotubes (inside of the nanotubes or in the interstitial channels between the tubes) exhibit a variety of phase transitions with the help of interactions between molecules in neighboring channels or tubes. Because the channels/tubes are widely separated, these transverse interactions are weaker than the (longitudinal) interactions within the same channel. The transition temperatures that result are therefore lower than those of typical two- or three-dimensional transitions of the same species of molecules. We discuss here the condensation transition of such a gas to form a liquid, expressing the transition behavior in universal form, where the reduced critical temperature $T_c^*$ is a universal function of the reduced transverse interaction.
I. INTRODUCTION

A growing literature of experiments, simulations and theory is devoted to the study of various gases adsorbed either inside or outside of bundles of carbon nanotubes. On the inside, adsorption may occur either within the tubes or in the interstitial channels (ICs) between tubes. On the outside, the adsorption of small molecules is believed to start in the grooves between nanotubes and then cover the surface with a film of increasing coverage. One of the most tantalizing aspects of this research is the possibility of observing one-dimensional (1D) or quasi-1D matter. By the term “quasi-1D”, we mean those phases for which the transverse interactions (between particles in adjacent 1D chains) play a non-negligible role in determining the phase behavior of systems that in some respect are 1D; in particular, the transverse interaction is essential to producing a genuine thermodynamic transition at nonzero temperature (T). In fact, all of these phases are 3D (since the particles of interest are highly constrained by the nanotube lattice), so there is some ambiguity in the choice of terminology.

Such quasi-1D phases can occur, in principle, within the tubes, within the ICs or in the grooves. Two kinds of transitions have been discussed theoretically: condensation and crystallization. Both kinds differ from their counterparts in 3D matter because of the extreme anisotropy of the ordered phase and the low values of the predicted transition temperatures, which are even lower than those of monolayer films. The reason for these differences is that the transverse interaction is much weaker than the longitudinal interaction (that within a given channel).

This paper describes universal behavior of the gas-liquid condensation transition in this environment, allowing one to deduce results for any particular system that is characterized by a set of assumptions. The key assumption is that the dominant interaction energy is that involving particles within a given channel, while the transverse interaction is much weaker. The longitudinal problem consists of a 1D fluid of particles interacting with Lennard-Jones (LJ) interactions:

\[ V_l(r) = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right] \]  

(1)

Here, as usual, \( \varepsilon \) and \( \sigma \) are the well-depth and hard-core diameter of the potential. The transverse interaction between molecules is written in the form known to describe long-range...
interactions in free space:

\[ V_t = -\frac{C_6}{r^6} \]  \hspace{1cm} (2)

The coefficient \( C_6 \) could be taken here as the free-space interaction coefficient of the particles, although there is theoretical indication that screening by the nanotubes alters this interaction significantly. One might assume, for example, that the same fundamental LJ interaction is responsible for the transverse and longitudinal interactions, in which case (from Eq. 1) \( C_6 \) assumes the value

\[ C_{6,LJ} = 4\varepsilon\sigma^6 \]  \hspace{1cm} (3)

A key aspect of the present paper is that we obtain the transition behavior in universal terms, so that the appropriate interaction parameters can be used to deduce quantities applicable to a system of special interest.

The outline of this paper is the following. The next section evaluates the transition behavior with two models. One describes the problem in terms of an anisotropic lattice gas model, which has been studied previously. The alternative model is a continuum description, in which case the equation of state is evaluated by treating the transverse interaction as a perturbation of the longitudinal problem. Perhaps surprising is the finding that the predicted transition temperatures are rather similar. Section III comments further upon the solution and related problems.

II. MODEL CALCULATIONS

In a preliminary work, we discussed \( C_{60} \) molecules adsorbed inside the nanotubes, a 1D system. If the interaction between molecules in neighboring tubes is considered, there is a transverse interaction that, even if it is weaker than the intrachannel interaction, is enough to drive a phase transition to a condensed phase.

Smaller atoms or molecules adsorbed in the interior of the tubes may have rich structures, depending on their size. In the case of \( \text{H}_2 \) and inert gases, the atoms are adsorbed first on the wall of the tube forming a shell, and after completion of the shell, for a higher chemical potential, the center of the tube starts to be filled. When that occurs, the coverage of the shell is similar to that of a monolayer on graphite and the system can be seen as a
superposition of a 1D gas constrained to the center (axial phase) and a thermodynamically inert solid shell covering the wall.

We find a qualitatively similar situation in the case of atoms in the interstitial channels. For example, as predicted in a previous work, small atoms or molecules like He, Ne or H$_2$ can be adsorbed in the interstitial channels of a bundle of nanotubes, forming a 1D gas, that would condense due to the interaction with atoms in other interstices of the bundle.

In either of the two cases, the purely 1D gas can be described by the equation of state for Lennard-Jones interacting particles,

$$
\frac{1}{a} = \frac{\int_0^\infty dz \ e^{-\beta[V(z)+zP_{1D}]} \ dz}{\int_0^\infty dz z \ e^{-\beta[V(z)+zP_{1D}]} \ dz}
$$

(4)

that expresses the 1D density, $N/L = 1/a$, in terms of the 1D line pressure $P_{1D}$ and $\beta = 1/(k_B T)$. Here $z$ is the coordinate along the channel, or axis of the tube.

The interaction with molecules in neighboring channels or tubes can be considered in a perturbative way, so the change in the free energy is given by

$$
\Delta F_{\text{inter}} = \frac{N\nu}{2a} \int_{-\infty}^\infty dz V_t[(b^2 + z^2)^{1/2}]
$$

(5)

Here $b$ is the separation between tubes or channels and $\nu$ is the number of nearest neighbor tubes or channels. For atoms inside the tubes, $b = 17 \ \text{Å}$ (for (10,10) tubes) and $\nu = 6$, since the tubes form a hexagonal lattice, while for IC atoms the lattice is honeycomb, with $\nu = 3$ and $b = 9.8 \ \text{Å}$. In the case when $b$ is sufficiently large that the interaction may be approximated by the asymptotic form $V_t(r) \approx -C_6/r^6$, the integration yields

$$
\Delta F_{\text{inter}} = -\nu N \frac{3\pi}{16} \frac{C_6}{b^6} \frac{1}{a}
$$

(6)

Including this term in the equation of state yields a relation for the shift of the 1D pressure proportional to $1/a^2$

$$
P(a, T) = P_{1D}(a, T) - \frac{\alpha}{a^2} \ , \ \alpha = \nu \frac{3\pi}{16} \frac{C_6}{b^6}
$$

(7)

As a consequence, the pressure as a function of the density exhibits a van der Waals loop at low temperature, indicating the presence of a phase transition from a dilute phase to a higher density phase. The critical temperature for this transition depends on the strength
of the transverse interaction, $\alpha$. In Fig. 1 (solid line) we plot the scaled critical temperature deduced from Eq. 7

$$T^*_c = \frac{T_c}{\varepsilon}$$

as a function of the reduced transverse interaction strength,

$$\alpha^* = \frac{\alpha}{\varepsilon\sigma}.$$  \hspace{1cm} (9)

Note that Fig. 1 is a universal curve, from which one can extract the critical temperature for any gas, adsorbed in either type of array of 1D channels. All the key information about the gas and array (i.e. $\varepsilon$, $\sigma$, $\nu$ and $b$) is included in the universal constant $\alpha^*$. For example, for He in an array of IC, $\alpha^*$ is $7.5 \times 10^{-3}$ resulting $T^*_c = 0.1$, while for He in the interior of the tubes, $\alpha^*$ is $9.5 \times 10^{-4}$ and $T^*_c = 0.075$.

Next, we study the system as an anisotropic lattice gas. The sites of the lattice are separated by a typical interatomic distance $a$ along the channels, and the channels form an array (hexagonal or honeycomb for the interior sites or interstitial channels respectively). Fisher proved that the critical temperature for an anisotropic Ising model in a cubic lattice has the form

$$k_B T_c = \frac{2J_t}{\ln(1/c) - \ln[\ln(1/c)]}$$ \hspace{1cm} (10)

where $J_t$ is the interaction along the channel, and $c = J_t/J_l$, where $J_l$ is the transverse interaction. This formula is valid only in the very anisotropic case, i.e. $c < 0.1$ and includes only nearest neighbors’ interactions. To adapt this model to our system, we choose $J_l = V_t(a)/4$ (the usual conversion from Ising model to a lattice gas), and

$$J_t = \eta \frac{\tilde{V}_t(b)}{4}$$ \hspace{1cm} (11)

where $\eta$ is the coordination number of the lattice ($3/2$ and $3$ for honeycomb or hexagonal, respectively) and $\tilde{V}_t = fV_t$ represents the interaction between an atom in one channel with $f$ atoms in a neighboring channel. We introduce the factor $f$ to account for the fact that if $b \gg a$, we count the transverse interaction with more than one atom in the neighboring channel. Actually, $f$ is proportional to $b/a$ and is calculated from an equation expressing the effective nearest neighbor interaction in terms of the net effect of all neighbors,
\[ V_t = \sum_i V_i[(b^2 + z_i^2)^{1/2}] \]  

where the sum is over all the atoms in neighboring channels, in positions \( z_i \) along the channel. If \( b >> a \), the sum can be approximated by the integral

\[
\frac{1}{a} \int_{-\infty}^{\infty} dz \, V_i[(b^2 + z_i^2)^{1/2}] = fV_i(b)
\]

with

\[
f = \frac{3\pi b}{8a}
\]

This factor, for example, equals 4.5 in the case of He in the interstitial channels, with \( a = \sigma \).

With this consideration, the factor \( c \) is identical to \( \alpha^* \).

In Fig. 1, dashed line, we plot the resulting critical temperature as a function of \( c = \alpha^* \). Note the similarity of the trends predicted with the two different approaches, as previously found for the particular case of C\(_{60}\). This occurs because this transition happens at a low value of \( T \), when the longitudinal correlation length is so long that the (essentially mean field) perturbation theory is expected to work\(^{17} \).

In Table I, we display the critical temperatures for some gases adsorbed inside the tubes or in the interstitial channels, according to perturbation theory and the lattice gas model. SF\(_6\) is included in the table but it is not clear whether it would form a 1D phase inside the tubes, even as an axial phase.

III. SUMMARY

We have found, with alternative models, the critical temperatures for an anisotropic fluid within a nanotube bundle. The resulting expression for \( T_c^* \) exhibits a universal dependence on the reduced interaction strength. Such transitions would be extremely interesting to find experimentally.

The present model makes a number of simplifying assumptions. The neglect of disorder (due to impurities and thermal vibrations) appears to be the most serious approximation. An additional assumption is the use of free space pair interactions for the numerical results,
omitting the effect of interaction screening by the tubes and elastic-mediation of the interaction due to dilation and deformation of the tube lattice.\textsuperscript{10}

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TABLE I: Reduced critical temperature $T^*_c = T_c / \varepsilon$ and reduced transverse interaction $\alpha^* = \alpha / (\varepsilon \sigma)$ for various gases adsorbed in the interstitial channels (IC) or inside the nanotubes (NT), calculated by perturbation theory ($T^*_{c, \text{pert}}$) or from the lattice gas model ($T^*_{c, \text{LG}}$). Values of $C_6$ entering in $\alpha^*$ were taken from Ref. 18 in the case of He, Ne, Ar, Kr and Xe. For the rest of the gases, a Lennard-Jones transverse interaction was assumed, with $C_6 = 4 \varepsilon \sigma^6$. The empty spaces in the table occur because large atoms or molecules are believed to be excluded from the ICs.
FIG. 1: Reduced critical temperature $T_c/\varepsilon$ as a function of the reduced strength $\alpha^*$, defined in the text, from a perturbative calculation (solid line) and lattice model (dashed line). Inset is an expanded version of the small $\alpha^*$ region.