Condensed Phases of Gases inside Nanotube Bundle

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Abstract:
Small molecules absorbed by nanotube bundles undergo temperature dependent transitions from ordered to disordered phases. Depending on thermodynamic condition one or two dimensional behavior is observed for those particles as well as dimensional cross overs. Here an overview of phase behavior for gases exposed to nanotubes is presented.

1 Introduction

A new form of carbon material discovered in 19991 is carbon nanotube. Carbon nanotubes are cylindrical tubes of typical radius of 5 and 10 A made of one or more layers of concentric layers of graphite. Their remarkable aspect ratio of 10^4 of the length of tubes to their radius allow the observation of the novel 1D behavior of matter, for the matter imbibed inside the tubes and the tubes themselves.

In the form of bundles (Fig. 1), (or ropes) they have a large surface area per gram of material. If it is presented to gases, they absorb gases extensively. The gas uptake can be stored in any of the three regions shown below. (see Fig. 1.)

The size of the nanotubes is such that many species of small atoms (diameter of order 3A) fit comfortabley within the tube. In the nanotube bundle geometry, the small atoms are even more strongly adsorbed in the narrow interstitial channels between than tubes than within them.

Molecules absorbed in different regions of nanotube bundle, undergo transitions from ordered to disordered quasi-1-dimensional phases. A crossover from 1D to 2D is possible as a function of temperature and coverage for different species.

Figure 2 presents the results of calculations of the uptake of various gases at different sites.

Here we explore the phases of the adsorbate present at each of these sites in a bundle of nanotubes.

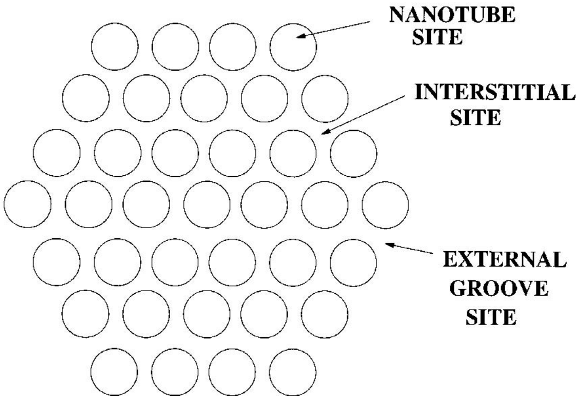

Figure 1: schematic view of a nanotube bundle and different sites of absorption.

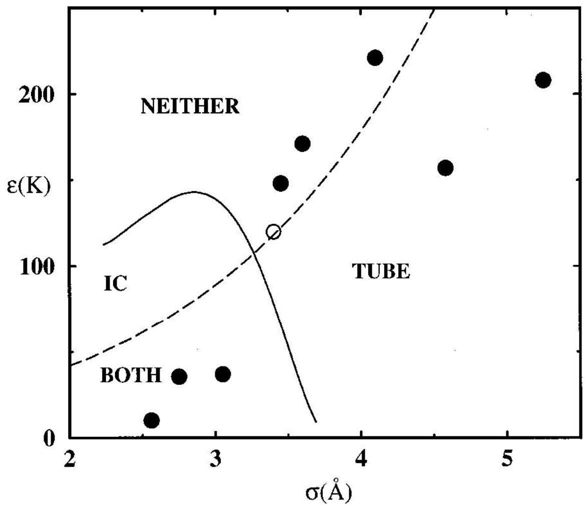

Figure 2: Location of the absorbed atoms or molecules within a bundle of tubes of radius 8A, as a function of Lennard-Jones parameters. Dots correspond to the sequence of increasing values of σ [1].

2 Particles in the tubes

Both small and large molecular species are seen to absorb strongly inside the nanotubes, in contrast to the intermediate size gases, CH_4, Kr, and Xe. This is a competition between adhesive and cohesive forces, between the gas molecules and the C atoms in the bundle. The number of molecules absorbed at each temperature varies a function of the thermodynamic parameters of the system. Condensation of the gas to liquid occurs as soon as the chemical potential of the molecules drops below μ_0, the chemical potential at saturated vapor pressure.

2.1 Ideal gas model

At low densities we may neglect the interaction between the particles and describe the system as free particles confined inside the tube [3]. We use the quantum mechanical energy spectrum of the individual particle confined in the tubes, and use the classical statistics to describe the thermal properties of the gas as a whole.

The classical ideal gas model assumes that the probability of a single particle having energy E is proportional to the Boltzman function, p(E) = exp (-βE), where $\beta^{-1} = k_B T$. The behavior of the system depends on n(E), the density of states, whose form should be determined for the particles inside the tube. Do to the symmetries of the system, the wave function of the system can be written as:

$\psi(\mathbf{r}) = L^{\frac{-1}{2}} e^{ikz} \psi_{n\nu}(r, \phi)$ and

$$E = \frac{h^2k^2}{2m} + E_{n\nu}$$

$\frac{h^2k^2}{2m}$ is the kinetic energy of the particles along z direction and $E_{n\nu}$ is the energy of the transverse motion. L is the tube length and ϕ is the azimuthal angle.

The lowest energy states of the system correspond:

$$\psi_{1\nu}(r,\phi) = f_{1\nu}(r)e^{i\nu\phi}$$

where ν is an integer.
Because of the small size of the tubes, the radial degrees of freedom have 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.
At very low T, only the 1D motion, corresponding to $\nu = 0$ is excited. As the temperature increases. the states with higher ν values also contribute and a 2D behavior is observed.

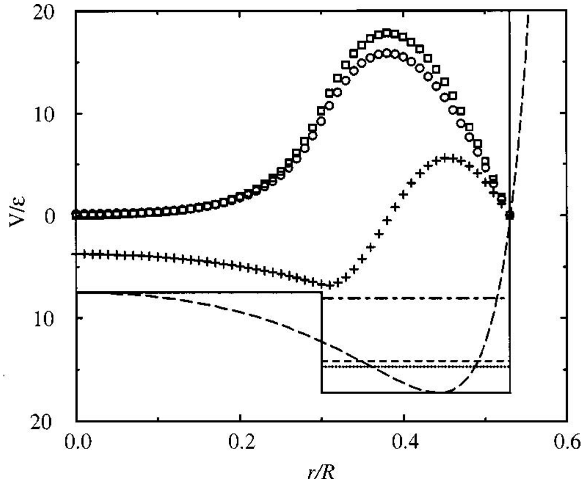

Figure 3: The model potential (—) and the true potential (–) for He inside a nanotube or R=5 A. The lowest energy values are shown. The wave functions shown correspond to ground state (o), first azinuthally excited state (4), and the first radially excited state (+) [3].

Figure below shows the specific heat per particles, for He atoms inside the single wall nanotubes, as a function of temperature. It can be seen that as the temperature increases the heat capacity increases towards the value for the two dimensional ideal gas Nk_B from the 1D value $\frac{Nk_B}{2}$.

The dimensionality cross over occurs at a value of T corresponding approximately to the first azimuthal excitation energy. The value of T depends on the nanotube radius, a greater R implies smaller azimuthal energy.

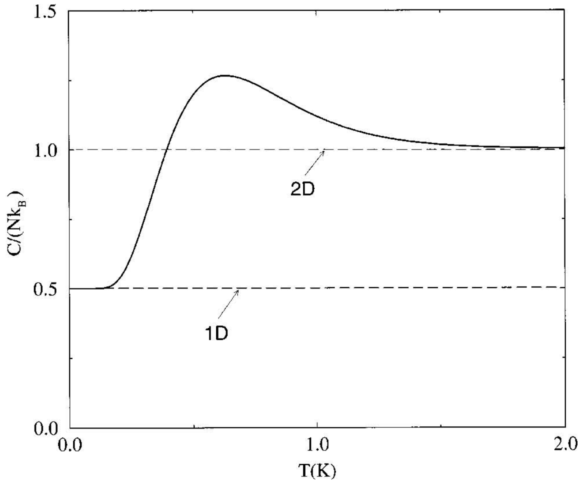

Figure 4: default

2.2 Collective behavior of atoms inside the nanotube

One particular property of the system is the existence of the crystalline phases (at high density) at finite T, inside the tubes. Atoms will form a cylindrical shell film coating the nanotube wall. Thermal excitations of these solids results in the appearance of the phonon-like collective modes. At low temperatures the heat capacity arising from the phonon modes, shows linear dependence on T, and as T increases, at high temperatures a quadratic temperature dependence is calculated.

This is analogous to the behavior of the ideal gas in 1 and 2 dimensions. If we characterize the phonon modes by their azimuthal variation, ν (which is a quantum number) and the spatial variations along z axis, q_z, long wave-length phonon modes correspond to the axial modes, having no angular variation. In these cases the excitation spectrum will be similar to those vibrations in 1 dimension. As the temperature increases the azimuthal modes also become excited and a 2D behavior is observed. Figure 5 shows the dimensional cross over of the heat capacity.

The cross-over temperature, where this effective dimensionality changes from 1 to 2, can be estimated as when the circumference of the cylinder containing the atoms becomes equal to the thermal wavelength, $2\pi R_{shell} = hc/k_B T$

Another feature is the condensation of the particles on the axis of the tube. This is similar to the capillary condensation and results in a 1D axial phase. (see Fig. 6)

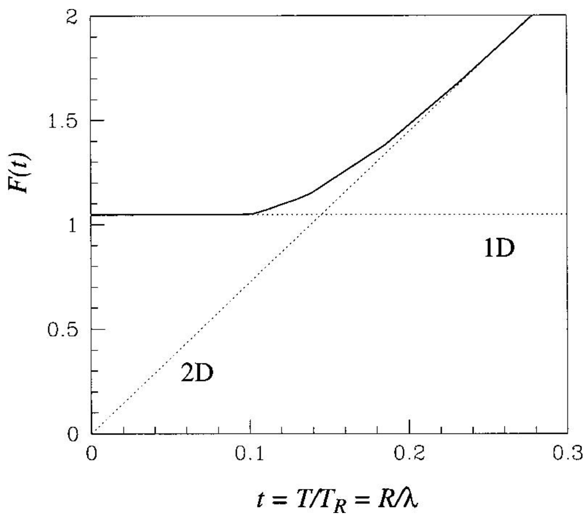

Figure 5: The dimensionless ratio of the heat capacity of phonons to temperature [3].

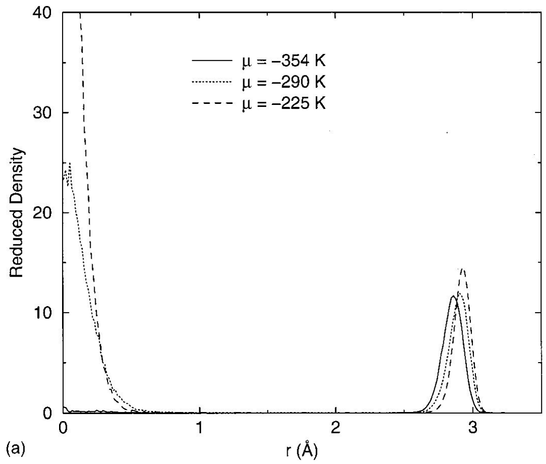

Figure 6: Density of hydrogen molecules at T=10K computed by Monte Carlo simulations, inside a nanotube of R=6A, for different values of chemical potential [1].

3 Gases within Interstitial Channels

Tiny atoms or molecules like He, Ne or H2 are strongly attracted to the interstices between the tubes; these spaces are sufficiently small that a purely 1D theory may be applicable, e.g., in the case of He atoms that are confined to a region of radius of R = 7 A, the wave function extends (significantly) only to 0.2 A from the axis.

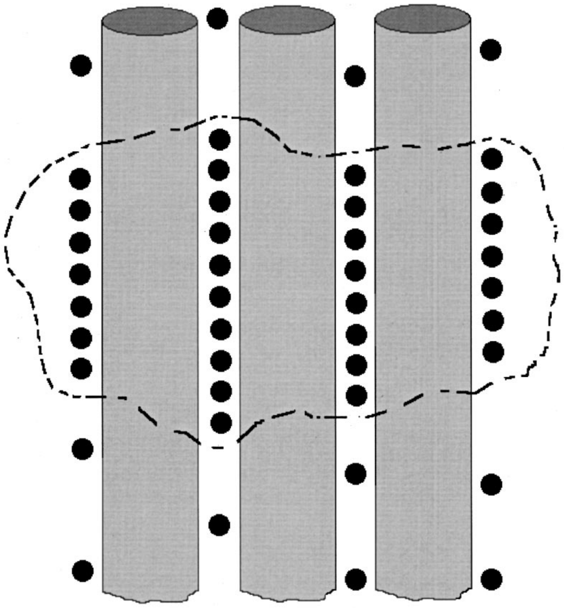

Figure 7: Anisotropic condensation of the adsorbate within interstitial channels.

For a 1D system, there is no phase transition at finite T. This is because any ordering in 1D will be disrupted by thermal fluctuations. So for a system consisting of single interstitial channel, there is no condensed phase at finite T. However, at T= 0, the phase transition may occur as a function of density. The interaction of the particles in adjacent interstitial channels is necessary for condensation at finite T. The interaction of the particles inside the channels can be described by Lennard-Jones potential,

$$V_l(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^1 2 - \left(\frac{\sigma}{r}\right)^6\right]$$

if this interaction is extended to the molecules in neighboring channels, there will be a condensation of these 1D chains to a 2D condensate. Since the separation between the interstitial channels is large (10 A), the interchannel interactions are quite weak and can be described by long-range interactions:

$$V_t = \frac{-C_6}{r^6}$$

where in this case (LJ potential)

$C_6 = 4\epsilon\sigma^6$

Figure 8 is shows the result of Monte Carlo calculations of He atoms inside a nanotube bundle [1]. The heat capacity is seen to correspond closely to a 1D system down to $k_B T/\epsilon = 0.25(\epsilon = 10.22$ K for He), after that the interacting system exhibits a phase transition (condensation of the anisotropic fluid)

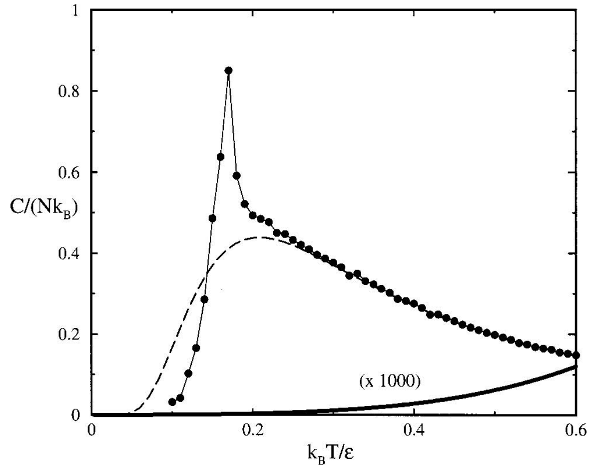

Figure 8: Specific heat as a function of Temperature relative to the interaction energy along the axis. Monte Carlo (points) calculations suggest a divergence (as in the theory). Dashed curve corresponds the case when interachnnel interactions are neglected. The broad solid line is the specific heat of the bundle of nanotubes [1].

This is an example where the dimensionality increases as the temperature decreases, in contrast to the previous cases where by decreasing the temperature the effective dimension of the system decreased. The transition temperature depends on the interaction parameters, and in fact the low transition temperatures for these species compared to their phase transition in bulk phases are a result of the extreme anisotropy of the interactions.

4 External Surface Adsorption

The external surface of the bundle can also adsorb molecules of different sizes. Several experiments have explored the behavior of gases adsorbed on the outside of nanotube bundles. The molecules are adsorbed first at the grooves, forming a 1D phase. As the coverage increases we see a discontinuous transition to the 3 stripe phase. This is due to the appearance of two new lines of particles parallel to the grooves. This is followed by the formation of a full layer of stripes, and then the bilayer formation. All these steps correspond to the discontinuous jumps in the coverage as the chemical potential increases. The properties of the matter after that point can be described similar to the wetting films on the graphite. Figure 9 shows the potential energy V(r) of Ar atoms on the external surface of a nanotube bundle, computed by summing empirical Lennard-Jones pair interactions between the molecules and the C atoms comprising the tube[3]. As it can be seen a deep well, corresponding to the grooves is the most favorable adsorption site. Ground canonical Monte Carlo simulations of different gases[3,7], using this simple potential (pairwise additive) show the existence of a second layer groove phase, following the monolayer completion (Fig. 10).

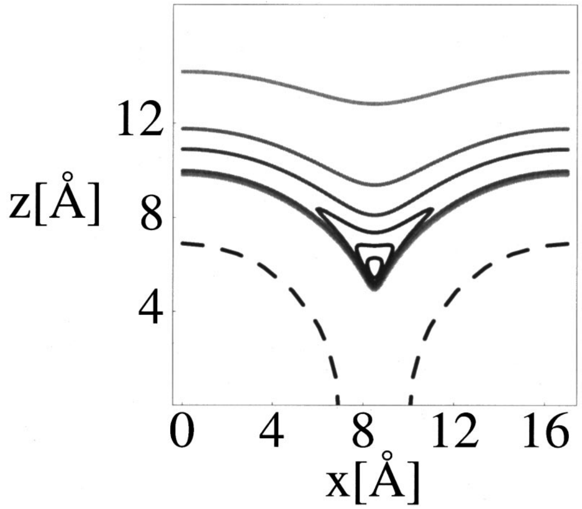

Figure 9: Groove confinement potential. Solid lines show equi-potential surfaces of an Ar atom, corresponding to the values V / ϵ = -25. -20. -15, -10, -5, -1, from darker to lighter. ϵ = 58 K. Dashed lines correspond to the cylindrical surface of the nanotube [1].

This simple model for the potential (pairwise additive) which assumes a perfect nanotube is in agreement with experimental data, and can explain some of the properties of the gases observed there. The number of particles adsorbed on the surface depends on the surface to volume ratio and varies as the inverse of the bundle radius. For a bundle of 50 tubes, roughly half of the available surface lies on the outer surface.

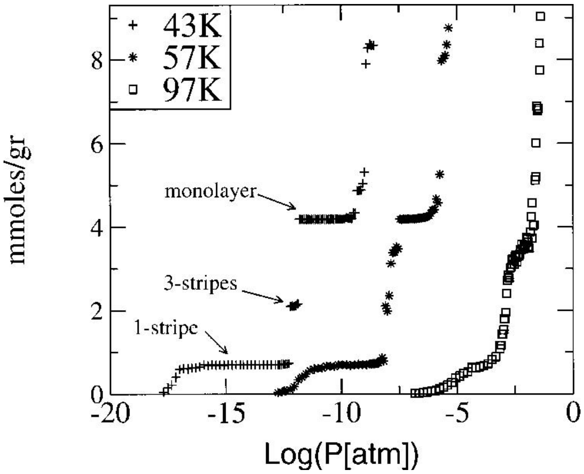

Figure 10: phase transition occuring within Kr atoms adsorbed on the external surface of a nanotube bundle, as function of pressure. The stable values of coverage correspond to striped phases, lying parallel to the grooves between external tubes [3].

5 Discussion

Here we have presented different phases of the absorbed gas molecules in a nanotube bundle and some of the interesting properties of the matter in the reduced dimensions have been explained by simple models. In all these models the nanotubes have been assumed to keep their own shape, and that they do not deform. In some cases, like the single particles inside the tubes, the particles have been treated classically, however at low temperatures these interaction may not be neglected. As it was seen in the paper both simulations and experiments can be used to study the physical properties of matter inside the nanotubes.

6 references

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