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Ordered phases of atoms adsorbed in nanotube arrays

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The low temperature properties of matter confined in an array of narrow one-dimensional channels are discussed. Weak interchannel interactions can stabilize a crystalline phase. The melting transition is expected to be continuous for both two- and three-dimensional arrays. Possible experimental realizations are suggested. Crystals of noble gas series elements confined inside 1 nm wide nanotube arrays are expected to be stable at temperatures up to 1 K.

The effect of geometric confinement or reduced dimensionality on the properties of matter has attracted much attention over the years. It is well known that fluctuations become increasingly important as dimensionality is reduced, making it impossible for one-dimensional systems with finite range interactions to order (except at zero temperature).[1] Steady progress in materials science provides an ever growing number of experimental realizations of one-dimensional matter. A prime example is an array of atoms confined inside carbon nanotubes or intercalated in the interstitial channels of a nanotube bundle.[2,3] Other interesting examples are alkane-urea inclusion compounds, in which guest alkane molecules are laterally confined, but retain axial mobility, inside subnanometer-sized one-dimensional channels in a crystalline urea structure.[4]

This paper investigates the possibility of the existence of a crystalline phase of atoms confined inside structureless one-dimensional channels that have macroscopic axial dimensions, but a nanometer-sized cross section, essentially forcing the guest atoms to line up in a row. The assumption is made throughout that the walls of the channels are smooth. (This assumption a priori excludes the possibility that registry effects stabilize a commensurate solid phase. We will discuss this point further below.) When the channels are bundled up in regular arrays, even exceedingly weak interchannel interactions can stabilize ordered phases. It has been argued recently that a transition into a weakly bound, highly anisotropic *commensurate* solid state is possible for helium atoms confined to the interstitial channels of carbon nanotubes.[5] The argument presented there applies more generally to other adsorbates and adsorbants. Here, we show that an additional state is possible, which has nontrivial one-dimensional *incommensurate* crystalline order along the axes of the tubes. Since the order parameter of this state is a scalar, its properties are markedly different from those of usual crystals in both two and three dimensions. In particular, melting is expected to be a continuous single-step transition in both two and three dimensions, and the melting temperature is proportional to the square root of the shear modulus, rather than to its first power. In view of the extremely small values of the shear modulus for these novel crystals, the square root dependency is important in making this state accessible to experiment.

We begin by considering a simple model of particles confined inside an array of parallel tubes, as depicted in Fig. 1. We assume that the size of each tube is such that no more than one atom is allowed per cross section of the channel. (This condition can be easily met in an experiment.) The figure may represent a flat two-dimensional array of nanotubes deposited on a surface, or a two-dimensional cross section, containing the axis of the tubes, of a three-dimensional array. (In a $3d$ array, the channel cross sections would occupy the sites of a honeycomb lattice, if the guest atoms are interstitially intercalated, or the sites of a triangular lattice, if the atoms are adsorbed inside the tubes.)

Unlike the usual condensed phases, where structure is determined primarily by packing constraints (i.e., hard core repulsion), the arrangement of atoms in adjacent channels is governed by the long range tail of the interatomic interaction. If this is attractive, as is normally the case, the atoms will tend to register in order to minimize the energy. In $2d$, for example, the preferred crystalline arrangement will be a rectangular, rather than triangular lattice.

Let us label the coordinate of the jth particle in the ith tube by $\vec{R}_{i,j}+\hat{z}u(i,j)+\vec{u}_{\perp}(i,j)$, $\vec{R}_{i,j}$ being a lattice coordinate. Let also a denote the lattice constant along the z direction, and b that in the transverse direction(s). The total potential energy can be written as

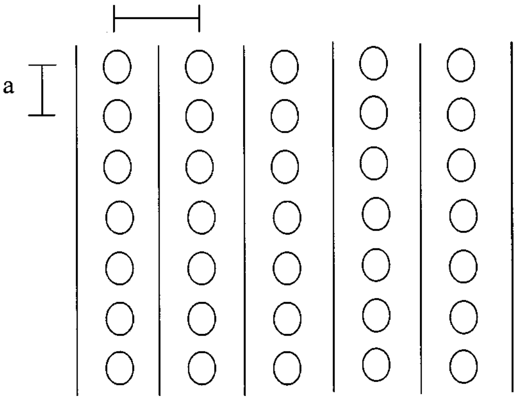

FIG. 1. Crystalline arrangement of guest atoms confined inside a host array of narrow channels. a is the lattice constant in the nontrivial direction. The value of b is determined entirely by the structure of the host.

$$U=\sum_{i,j} v(|\vec{R}_{i,j}-\vec{R}_{i,j-1}+\hat{z}u(i,j)-\hat{z}u(i,j-1)+\vec{u}_{\perp}(i,j) -\vec{u}_{\perp}(i,j-1)|)+v(|\vec{R}_{i,j}-\vec{R}_{i-1,j}+\hat{z}u(i,j)-\hat{z}u(i-1,j) +\vec{u}_{\perp}(i,j)-\vec{u}_{\perp}(i-1,j)|)+w(|\vec{u}_{\perp}(i,j)|), \tag{1}$$

where v is an interparticle potential (e.g., the Lennard-Jones interaction). This interaction can be treated as nearest neighbor without loss of accuracy. In the transverse direction, the particles are confined within each tube by a stiff harmonic potential, w. In the low temperature regime that we are concerned with here, we can regard the transverse degrees of freedom $u_{\perp}$ as frozen out.

To make connection with elasticity theory,[6] we use a continuum approximation, valid in the long wavelength limit. The effective Hamiltonian can be written as a function of the scalar displacement u only:

$$U=U_0+\frac{1}{2}\int d^{d-1}r_{\perp}dz\left[\lambda\left(\frac{\partial u}{\partial z}\right)^2+\mu\left(\frac{\partial u}{\partial r_{\perp}}\right)^2\right], \tag{2}$$

where the elastic constants

$$\lambda=\frac{v''(a)a^2}{b^{d-1}a}; \quad \mu=\frac{v'(b)b}{b^{d-1}a} \tag{3}$$

are reminiscent of the bulk and shear moduli of standard isotropic elastic theory.[7] To determine the stability of the crystalline phase in two and three dimensions, we examine the fluctuations of the displacement field u.

$2D$. Order in two-dimensional crystals is characterized by a diffraction pattern displaying algebraic peaks, rather than by sharp Bragg peaks.[8] This is also true for matter in two-dimensional arrays of nanotubes, where the broadening of the structure factor peak at reciprocal lattice vector $2\pi m/b$, $2\pi n/a$ is given by

$$S(\vec{q})\sim|p|^{-(2-\eta)}, \tag{4}$$

with $p\equiv\sqrt{(q_x-2\pi m/b)^2+\sqrt{\lambda/\mu}(q_z-2\pi n/a)^2}$ and the exponent is

$$\eta=\frac{2\pi T}{a^2\sqrt{\lambda\mu}}. \tag{5}$$

We expect (quasi)-long-range order to be unstable to unbinding of dislocation pairs.[8] Dislocations arise because of the constraint, which implicitly accompanies Eq. (2), that the line integral of the displacement around a closed contour must be an integer multiple of the lattice spacing a:[6]

$$\int\frac{\partial u}{\partial r_j}dr_j=-na. \tag{6}$$

A dislocation can be visualized as a missing semi-infinite string of atoms perpendicular to the direction of the tubes (Fig. 2). Note that the Burger's vector is necessarily parallel to the direction of the tube. This is a direct consequence of the fact that the dynamical variable of the model, u, is a scalar displacement. From this, it follows that this crystal melts, in two dimensions, *through a one-step process*, a continuous vortex unbinding transition, qualitatively analogous to the superfluid-to-normal transition in helium films. This behavior is unusual. For conventional 2D crystals, melting is predicted to happen through a *two-step* process:[8] dislocation unbinding that produces a hexatic phase with long range orientational order, followed at higher temperature by disclination unbinding into the isotropic liquid phase.

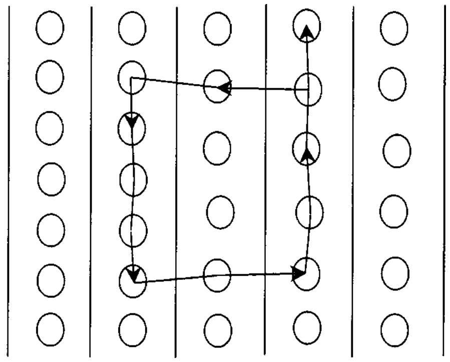

FIG. 2. Schematic depiction of a dislocation. Note the failure of a contour drawn around the dislocation core to close.

The melting temperature in our model is given by

$$T_{2D}=\frac{\sqrt{\lambda\mu}a^2}{8\pi}, \tag{7}$$

so that the exponent η, just below the transition, takes on, as usual, the universal value $\eta(T_{2D}^-)=1/4$. A similar transition was recently predicted for a 2D colloidal crystal subject to a 1D periodic potential.[9]

$3D$. The melting transition in three-dimensional arrays is expected to be continuous, unlike in conventional 3D crystals. Qualitatively, a continuous transition should be expected because of the geometric constraints forcing the particle to move in one dimension. As a consequence, no structural rearrangement is possible upon melting (i.e., the *local* structure of the liquid is identical with that of the crystal, as happens in 2D), so that no abrupt density change occurs upon melting.[10] The melting temperature can be estimated by the Lindemann criterion.[11] We evaluate the mean square displacement of the particles along the axis of the tubes:

$$\langle u^2\rangle\equiv\frac{1}{V}\int\frac{d^3k}{(2\pi)^3}\langle u_k u_{-k}\rangle=\frac{k_{\mathrm{B}}T}{4b\sqrt{\mu\lambda}}, \tag{8}$$

where the high-k cutoff in the transverse direction has been set to π/b. Following the Lindemann criterion, we assume the crystal to melt when the root mean square displacement is equal to a fraction c_L of the lattice constant a. This yields the melting temperature

$$T_{3d}=4c_L^2\sqrt{\mu\lambda}ba^2. \tag{9}$$

The system-dependent Lindemann constant c_L typically ranges in the interval $0.1<c_L<0.3$.

To make quantitative predictions for noble gases, we make a connection to the known values of the melting temperature of their standard 3D crystalline phase. This can be done in a straightforward manner, if one approximates those crystals as isotropic elastic media. In that case, the Lindemann criterion becomes

$$T_{\mathrm{iso}}=\frac{12\pi}{35}c_L^2a^3E, \tag{10}$$

where, for isotropic media, Young's modulus $E=2.5\lambda$. We assume a Lennard-Jones potential,

$$v(r)=4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12}-\left(\frac{\sigma}{r}\right)^{6}\right], \tag{11}$$

for which it is known that $E\sim70\epsilon/\sigma^3$.[12] Thus, the Lindemann criterion predicts that $T_{\mathrm{iso}}\simeq0.7\epsilon$, with a value of $c_L=0.1$ and $a\simeq\sigma$. This prediction is in very good agreement with the experimental values of $T_{\mathrm{iso}}/\epsilon=0.67$, 0.68, 0.52, 0.70 for Ne, Ar, Kr, and Xe, respectively.[13]

Returning to the weak crystalline phase in an array of nanotubes, we find an anisotropy parameter c from Eq. (3) (we put $\sigma=1$):

$$c=\frac{\mu}{\lambda}=-\left(\frac{a}{b}\right)^{6}\frac{(2/b^6)-1}{(26/a^6)-7}\simeq\frac{1}{20}\left(\frac{a}{b}\right)^{6}. \tag{12}$$

Remembering that λ is related to the isotropic Young's modulus of the 3D Lennard-Jones crystal by $\lambda=0.4(b/a)^2E$, we arrive at the prediction

$$T_{3D}=1.5\sqrt{c}\,\frac{a}{b}T_{\mathrm{iso}}\simeq\frac{1}{3}\left(\frac{a}{b}\right)^{4}T_{\mathrm{iso}}. \tag{13}$$

Coordination effects are expected to raise this value by a factor of $\sqrt{z/2}$, z being the number of nearest neighbors. For single wall nanotubes with diameter $d=10$ Å, we can put $b=12$ Å, and we obtain a melting temperature of about 0.3 K for interstitial Ne atoms and 1.2 K for Xe atoms adsorbed inside the tubes. More polarizable molecules, adsorbed inside nanotubes, would form stable crystalline states at higher temperatures. For example, for C_{60} buckminster fullerene adsorbed inside 1.5-nm-wide tubes,[14] we find a melting temperature of about 110 K in 3D, using the LJ parameters $\epsilon=2300$ K and $\sigma=9.2$ Å.[15]

It was recently pointed out that the interchannel interactions of atoms adsorbed interstitially within nanotube bundles should stabilize a weakly bound condensed phase.[5] The condensation temperature was estimated from the transition temperature of the strongly anisotropic lattice gas model, which yields

$$T_c=\frac{1}{2}\,\frac{v(a)}{\ln(1/c_l)-\ln[\ln(1/c_l)]}, \tag{14}$$

provided $c_l\leqslant0.1$. (Note that the anisotropy parameter has a different value in the liquid state, and is given by $c_l=v(b)/v(a)\simeq(a/b)^6$, again ignoring a lattice-dependent coordination correction.) For $c_l=0.1$, the condensation temperature is a sizable fraction of the Lennard-Jones parameter, $T_c\sim\epsilon/3$, that is, over an order of magnitude higher than the melting temperature T_{3D}. (Stronger anisotropy has a relatively small effect on T_c.) For comparison, the liquid-gas critical temperature of the unconfined bulk system is less than twice as high as the melting temperature.[13]

A subtle but important observation is in order. A lattice gas model, such as that proposed in Ref. 5, by construction can predict only one transition. This transition is often identified with a gas-liquid transition. However, the condensed phase of a lattice gas model has a built-in registry with the underlying lattice. Thus, the identification of the condensed phase with a (highly anisotropic) liquid is unambiguous only in the smooth channel approximation, on obvious physical grounds. In the presence of strong substrate corrugation, it might well be interpreted as a transition into a *commensurate* state, as is proposed in Ref. 5. In the present work, we have considered atoms trapped in smooth channels, showing the presence of a genuine *incommensurate* crystalline phase at temperatures significantly lower than the lattice gas condensation temperature T_c. Registry effects could play an important role in real systems, noticeably in the case of noble gas atoms in carbon nanotubes. For reference, all noble gases except Ar are known to form commensurate 2D solids on graphite in some pressure range.[16] In this regard, the qualitative difference between Ar and Kr is quite striking in view of the very small difference in the LJ diameter. This fact underscores that it will be very difficult to make accurate predictions without taking into account the quantitative details of each system. These would include not just the interatomic potentials, but also the precise structure of the host channels (e.g., the chirality of the nanotubes).

Finally, we comment on quantum effects, which have been ignored so far. Their importance can be gauged by evaluating the mean square fluctuation of u due to the zero point motion. Quantization of the Hamiltonian [Eq. (2)] leads to the following estimate, valid for large anisotropy:

$$\frac{\langle u^2\rangle_0}{a^2}\simeq\frac{0.08}{\sigma(\text{Å})\sqrt{\epsilon(\mathrm{K})A}}\ln\left(\frac{1}{c}\right), \tag{15}$$

where A is the atomic number. The values of $\sigma\sqrt{\epsilon A}$ are 16.5, 74.6, and 241 for He, Ne, and Ar, respectively. Although anisotropy increases the importance of quantum fluctuations, the dependence is logarithmic and is not expected to destabilize the crystalline phase, certainly not for Ar and likely not for Ne.

In summary, we have investigated the low temperature behavior of atoms adsorbed in an array of one-dimensional channels with nanometer-sized cross section. Weak interchannel interactions can stabilize a phase that has crystalline order in the direction of the channels. The estimated melting temperature for these novel crystals suggest that they should be well within experimental reach in several systems.

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