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## New Phase-Transition Phenomena in Thin Argon Films\*

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A density-functional theory capable of predicting free energies and spatially dependent number densities of simple classical fluids is applied to the case of argon films in the presence of a solid carbon dioxide substrate. For pressures less than the saturated vapor pressure, a new phase transition for which the order parameter is the film thickness is described. The phases are the usual unsaturated film and a one- or two-atomic-layer structure localized at the argon-CO<sub>2</sub> interface.

In this Letter we present the results of calculations of free energies and density profiles of thin argon films in the presence of a model carbon dioxide substrate which interacts with argon via a Lennard-Jones (6-12) pair potential. We find that for given pressure  $P < P_0(T)$ , the saturated vapor pressure at temperature  $T$ , two different film phases can occur. One is an unsaturated liquid film whose thickness  $t$  increases monotonically in accord with the well-known relation<sup>1</sup>  $t^{-3} \sim \ln[P_0(T)/P]$  as  $P$  approaches  $P_0(T)$  from below. The other is a very thin film having a thickness on the order of one or two atomic layers and which possesses considerable structure. When stable, this film is rather insensitive to changes in  $P$  and  $T$ . To distinguish the second type of film from the first, we shall call it an adsorption layer (AL).

A brief qualitative description of the physics is best posed in terms of adsorption isotherms along which  $0 < P < P_0(T)$ . For  $T_{cF} < T < T_c$  ( $T_c$  is the liquid-gas critical temperature), the thickness of the film grows continuously as  $P$  increases, becoming infinite at  $P = P_0(T)$ ;  $T_{cF}$  is the critical temperature for the new phase transition reported here. Then, for  $T_{AL} < T < T_{cF}$ , the AL is stable with respect to other structures at small  $P$  in that it possesses the smallest grand-

canonical free energy. As  $P$  increases, a point is reached at which the AL becomes less stable than a true film structure, which in general has a thickness considerably larger than that of the AL. For higher pressures up to  $P_0(T)$ ,  $t$  again increases in accord with the relation  $t^{-3} \sim \ln[P_0(T)/P]$ . Finally, for  $T_3 < T < T_{AL}$ , the adsorption layer is the only stable structure, and the usual unsaturated film never appears;  $T_3$  is the temperature at the argon triple point. The  $T$ - $t$  diagram of Fig. 1 summarizes this rather striking behavior;  $t$  is precisely defined by (4).

These results have been obtained using a density-functional technique recently developed by Ebner, Saam, and Stroud.<sup>2</sup> The theory is designed to describe nonuniform, classical Lennard-Jones (6-12) systems. The principal entity in the theory is the Helmholtz free energy  $F[n]$ , which is a nonlocal functional of the particle density  $n(\vec{r})$ . In a given physical situation, minimization of

$$\Omega[n] = F[n] + \int d^3r [V_{\text{ext}}(\vec{r}) - \mu] n(\vec{r}) \quad (1)$$

with respect to variations in  $n(\vec{r})$  yields an equation determining  $n(\vec{r})$  in the presence of the external potential  $V_{\text{ext}}(\vec{r})$  for fixed  $T$  and chemical

potential  $\mu$ . The explicit form of  $F[n]$  is

$$F[n] = \int d^3r f(n(\vec{r})) + \frac{1}{4}kT \int d^3r d^3r' C(\vec{r} - \vec{r}'; \bar{n}) [n(\vec{r}) - n(\vec{r}')]^2, \quad (2)$$

where  $f(n)$  and  $C(\vec{r} - \vec{r}'; n)$  are the free-energy density and the direct correlation function of a uniform system with density  $n$ . Also,  $\bar{n}$  is a non-local average density chosen here to be  $\bar{n} = \frac{1}{2}[n(\vec{r}) + n(\vec{r}')]$ . Both  $f$  and  $C$  have been calculated from solutions of the Percus-Yevick equation for a Lennard-Jones (6-12) fluid. A detailed discussion of (2) is given in Ref. 2. Suffice it to say here that  $F[n]$  is exact in the limit of small density variations and has (within the Percus-Yevick approximation) been applied with considerable success to calculations of the surface tension of liquid argon as a function of temperature.

We have chosen  $V_{\text{ext}}(\vec{r})$  as the potential due to a continuum of  $\text{CO}_2$  atoms in the half-space  $z < 0$  interacting with the argon atoms via a (6-12) potential. Integration over the continuum of substrate atoms produces a (9-3) potential which is<sup>3</sup>

$$V_{\text{ext}}(z) = 4\pi\epsilon_{0w}n_w\sigma_w^3 \left[ \frac{1}{45} \left( \frac{\sigma_w}{z} \right)^9 - \frac{1}{6} \left( \frac{\sigma_w}{z} \right)^3 \right], \quad (3)$$

where  $\sigma_w$  and  $\epsilon_{0w}$  are the range and depth parameters of the (6-12) potential while  $n_w$  is the effective  $\text{CO}_2$  atomic density. We have chosen<sup>4</sup>  $\sigma_w = 3.727 \text{ \AA}$ ,  $\epsilon_{0w}/k = 153 \text{ K}$ , and  $n_w\sigma_w^3 = 0.988$ ;  $k$  is the Boltzmann constant. An exact minimization of (1) produces a nonlinear integral equation for  $n(z)$ . Rather than attempt to solve that equation, we have minimized  $\Omega[n]$  by parametrizing  $n(z)$  and varying the parameters. Because the trial  $n(z)$  is a carefully chosen algebraic form contain-

ing ten adjustable parameters,<sup>5</sup> we have considerable confidence in the minima obtained in this way.

The results are presented in the three figures;  $T$  is in units of  $\epsilon_0/k = 119.76 \text{ K}$ ; length, in units of  $\sigma = 3.405 \text{ \AA}$ ; and  $n$ , in units of  $\sigma^{-3}$ . Here  $\epsilon_0$  and  $\sigma$  are the depth and range parameters of the argon (6-12) potential. The characteristic temperatures for this system are  $T_c = 1.3$  (in the Percus-Yevick approximation),  $T_{cF} = 0.92$ , and  $T_{AL} = 0.77$ . Also,  $T_3 = 0.7$  is an experimental result.

A representative set of results for  $T_{cF} < T < T_c$  is shown in Fig. 2, for which  $T = 1.1$ . The various curves are labeled by the asymptotic vapor density  $n_v$  far from the film rather than by the pressure  $P_v$ ; the latter differs little from the ideal-gas pressure obtained via use of  $n_v$ . At the phase-separation curve  $n_v = n_{vp}(T)$  which is 0.04736 at  $T = 1.1$ . Note the increasing film thickness as  $n_v \rightarrow n_{vp}$  [or, equivalently, as  $P_v$  approaches  $P_0(T)$  from below] and the considerable structure in the films near the substrate. The structure is, of course, expected on physical grounds. Figure 3 shows the results of calculations at  $T = 0.9 < T_{cF}$ ;  $n_{vp} = 0.01033$  at this temperature. The curves at  $n_v = 0.0099$  and 0.0101 are for structures in that part of Fig. 1 where films are stable. The curves labeled 0.0090, 0.0092, and 0.0095 are stable AL's. The transition from stable AL to stable film takes place at  $n_v = 0.0097$ . Both the AL and

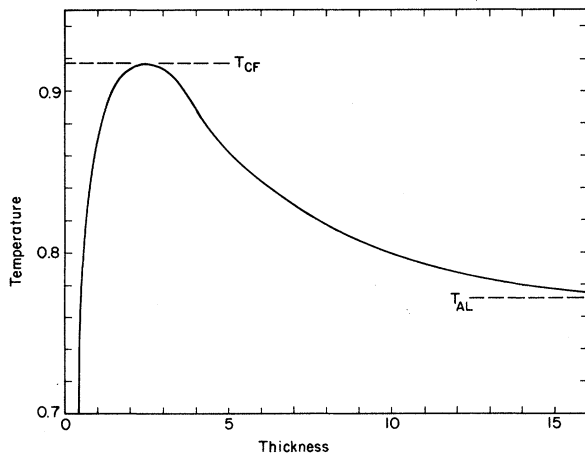


FIG. 1. The temperature-thickness diagram for argon adsorbed on a  $\text{CO}_2$  substrate;  $T$  is in units of  $\epsilon_0/k = 120 \text{ K}$  while the unit of thickness is  $\sigma = 3.405 \text{ \AA}$ .

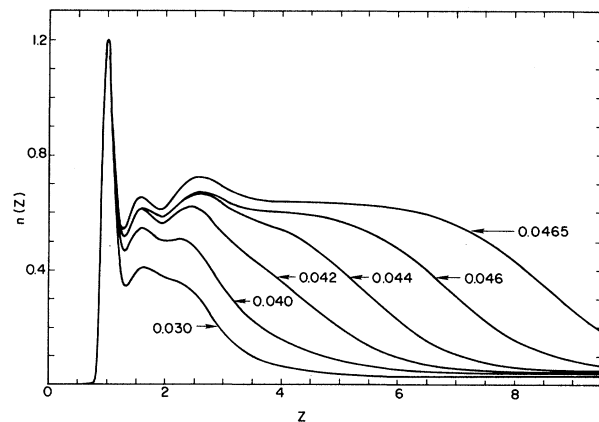


FIG. 2. Argon-film profiles at  $T = 1.1\epsilon_0/k > T_{cF}$  for argon-vapor densities between 0.03 and 0.0465; the density is in units of  $1/\sigma^3$  and  $z$  is in units of  $\sigma$ . Each curve is labeled by the value of  $n_v$ .

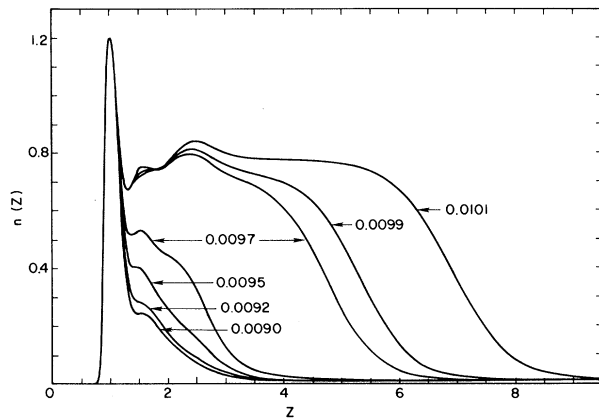


FIG. 3. Argon-film profiles at  $T = 0.9\epsilon_0/k < T_{cF}$  for argon vapor densities between 0.009 and 0.0101; the density is in units of  $1/\sigma^3$  and  $z$  is in units of  $\sigma$ . Each curve is labeled by the value of  $n_v$ .

film profiles are shown in Fig. 3 for this value of  $n_v$ . These structures both have the same value of  $\Omega[n]$  and they are at local minima of the free-energy functional for the given values of  $\mu$  and  $T$ . In order to learn something about the free-energy barrier separating these two profiles in the space of configurations, we have calculated  $\Omega$  along a path specified by a linear interpolation of the ten parameters in  $n(z)$  between the values taken on in the two equilibrium configurations. The barrier height is  $\Delta\Omega = 0.020\epsilon_0/\sigma^2$ . It would naturally decrease with increasing  $T$  and vanish at  $T = T_{cF}$ .

The thickness  $t$  in Fig. 1 has been calculated for each  $n(z)$  as

$$t = \int_0^\infty dz [n(z) - n_v]/n_l, \quad (4)$$

where  $n_l$  is the liquid density at the liquid-gas coexistence curve for the temperature in question.

A qualitative understanding of this new phase transition<sup>6</sup> is obtained by examining the major contributions to the difference between the free energies of the AL and of the film. Relative to the AL, the film has a positive free energy arising from its surface tension and a negative free energy coming from its interaction with the attractive part of the external potential. Also, the free energy of that portion of the film which has approximately a constant density of order  $n_l$  is larger than the free energy of the AL in the same region. Relative to the film, the AL has an important negative free energy arising from the negative short-range part of the correlation function  $C$ , there being relatively fewer atoms in the

AL on the vapor side of the large peak in  $n(z)$ . As a consequence of these facts, one can make several predictions. Increasing the strength of the attractive wall-substrate potential favors the film configuration (relatively weak potentials are required for the existence of the phase transition). Further, an increase in  $T$  decreases the surface tension and thus favors the film configuration. Finally, increasing  $n_v$  or  $P_v$  decreases the free-energy difference between liquid and vapor and hence also favors the film configuration. It should be recognized, however, that this simple picture breaks down for very thin film configurations in which a distinction between surface and bulk effects becomes impossible.

It is important to point out that the large peak in  $n(z)$  near the wall is virtually the same for all cases shown in Figs. 2 and 3 (as well as for all other calculated profiles). As a consequence, the contribution of this feature to  $\Omega$  is rather independent of the important variables in the problem—and fortunately so, for our theory is least trustworthy in the region of  $z$  where the peak occurs. There are two reasons. First, the density at the top of the peak exceeds the density  $n_{s3} = 0.966/\sigma^3$  of solid argon at the triple point. It is thus likely that the first layer of argon is solid, a feature not included in our theory.<sup>7</sup> Second, the smoothing of the  $\text{CO}_2$  substrate inherent in (3) certainly has its largest effect on the first layer of argon. Both of these simplifications affect the various film structures and energies in the same way. Our central conclusions are based on free-energy differences and are therefore not strongly dependent on these two flaws in our theory.

We conclude with a brief summary and some further general remarks. We have presented here calculations of argon-film profiles and free energies given a solid  $\text{CO}_2$  substrate. Although the calculations are approximate, they are made from first principles since  $F[n]$  is obtained directly from a pair potential. A prediction of our theory is a striking new phase transition for which the order parameter is the film thickness; the two phases are the ordinary unsaturated film and the adsorption layer, a structure which is roughly two monolayers thick and which changes relatively little with  $P$  and  $T$ . The  $\text{CO}_2$  substrate was chosen because its interaction with argon is sufficiently weak and also because it remains solid throughout the temperature range of interest. We remark that our theory has implications with regard to the phenomenon of wetting; in particular, it is easy to show that the argon- $\text{CO}_2$

contact angle will be greater than zero for  $T < T_{AL}$ . Careful measurements of adsorption isotherms would appear to provide the simplest means of testing our predictions. Neutron scattering experiments could, in principle, provide a wealth of detail about  $n(z)$ .

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<sup>1</sup>See, e.g., J. G. Dash, *Films on Solid Surfaces* (Academic, New York, 1975).

<sup>2</sup>C. Ebner, W. F. Saam, and D. Stroud, *Phys. Rev. A* **14**, 2264 (1976).

<sup>3</sup>Density profiles for bulk superfluid He<sup>4</sup> in the presence of such a potential are reported by C. Ebner and W. F. Saam, in *Proceedings of the Fourteenth International Conference on Low Temperature Physics*, edited by M. Krusius and M. Vuorio (American Elsevier, New York, 1975), Vol. I, p. 447.

<sup>4</sup>The potential parameters are such that the hard-core diameter is the mean of the CO<sub>2</sub> and argon hard-core diameters while the van der Waals attraction is equal to the square root of the product of the argon and CO<sub>2</sub> van der Waals attractions. The argon interaction was chosen as in Ref. 2 while the CO<sub>2</sub> potential was taken from J. A. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954), p. 1111. Finally,  $n_w$  is the number density of solid CO<sub>2</sub> at  $T = 100$  K as reported by

O. Maass and W. H. Barnes, *Proc. Roy. Soc. London, Ser. A* **111**, 224 (1926).

<sup>5</sup>The trial function used is

$$n(z) = \left[ \frac{\beta}{\exp[\gamma(z - \delta)] + 1} + \sum_{j=1}^5 \theta_j z^{j-1} \exp(-\epsilon z^2) + n_w \right] \times \exp\left(-\frac{\alpha z^{-9}}{T}\right),$$

where  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ ,  $\epsilon$ , and the five  $\theta_j$ 's are the variational parameters. This function  $\sim \exp(-\alpha z^{-9}/T)$  for small  $z$ ; it can oscillate by virtue of the power series; and, for the case of relatively thick films,  $\beta + n_w$  is the density of the film,  $\delta$  is approximately its thickness, and  $1/\gamma$  is the width of the transition region between the liquid film and the vapor which has density  $n_w$ .

<sup>6</sup>The possibility of such a transition appears to be hinted by L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Addison-Wesley, Reading, Mass., 1969), p. 469. This material is not contained in the 1958 edition.

<sup>7</sup>M. Chester, D. F. Brewer, L. C. Yang, and K. A. Elinger, *J. Phys. C* **7**, 1949 (1974) present a phenomenological local density-functional theory of adsorbed films. This theory uses the pressures at which liquefaction and solidification occur in the bulk to determine the location of the solid-liquid and liquid-gas interfaces in the film. The density profile of the adsorbate cannot be found using this formalism; interestingly, however, it predicts that a helium film adsorbed on Grafoil will have one or two solid atomic layers at its base—a result similar to what we have found for argon on CO<sub>2</sub>.

## Shubnikov-de Haas Oscillations in a Semiconductor Superlattice\*

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We have observed Shubnikov-de Haas oscillations associated with the quantum sub-bands created in superlattices made of periodic layers of GaAs and Ga<sub>1-x</sub>Al<sub>x</sub>As. By controlling the periodic potential profile, a variety of sample with sub-bands of different degrees of two-dimensionality have been prepared for investigation. The observed oscillatory behaviors agree with those predicted from the Fermi surfaces calculated theoretically on the basis of the superlattice configuration and the electron concentration.

The investigation of quantum sub-bands has been one of the major objectives in the studies of a semiconductor superlattice—a periodic structure made of alternating, ultrathin layers of two semiconductors. Experiments reported to date,<sup>1,2</sup> including the recent resonant Raman scattering measurements,<sup>3</sup> have largely established the existence of such sub-bands, their energy positions, and their influence on the dynamics of electrons moving perpendicularly to the layers. In this Letter, we report the first observation of magnetoquantum oscillations (Shubnikov-de Haas

effect) in superlattices with the current flowing in the plane of the layers. The superlattice provides a unique medium where the bandwidths of the sub-bands can be controlled by selecting the barrier and well thicknesses as well as the barrier height. The observed oscillations manifest the electronic sub-band structure, which becomes increasingly two-dimensional in character as the bandwidths is narrowed.

Figure 1 illustrates three sub-band structures (A), (B), and (C), with a superlattice energy diagram shown schematically in the upper panel: