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Characteristics of adsorbed films

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Discussions of wetting and clustering in van der Waals films, given in the authors' previous papers, are extended and corrected.

In two previous papers[1,2] different types of behavior of adsorbed films were discussed. For three principal types the chemical potential, free energy, and vapor pressure are shown in Figs. 1–3 as functions of the adsorbed amount in a uniform layer. In type 1 the adsorbed amount per unit surface area n rises smoothly with pressure, tending to infinity at the bulk vapor pressure. In type 2, n tends to a finite limit n_1 as the bulk vapor pressure in reached and further adsorbate is in the form of bulk phase, either in droplets on the surface or elsewhere. In type 3 no adsorption takes place before the bulk vapor pressure is reached. In this paper we add some further relevant comments.

(1) The first comment relates to type 3. This requires the absence of any net attraction on adsorbate molecules near the substrate surface. But the van der Waals forces between a molecule and the substrate are necessarily attractive. Dzyaloshinskii *et al.*[3] argue that the force between an adsorbed film and a substrate can in certain circumstances be repulsive, but this result applies only to film thicknesses for which continuum electrodynamics is a good approximation, and not to a monolayer or less. At sufficiently low densities the interaction must be attractive. If the strength and range of the attraction are such as to give rise to a bound state at the surface, the chemical potential must contain at any finite temperature a term proportional to log n, with a negative coefficient; hence, a small amount is adsorbed at any pressure. Even if there is no bound state, the density of molecules in the attractive region will be greater than in the body of the vapor, so that there must be a surface layer containing a number of molecules in excess of those in the vapor. It would seem, therefore, that type 3 is not a realistic possibility.

Yet there exist cases in which the isotherm resembles that in Fig. 3. This is not a contradiction, because the maximum amount adsorbed below the bulk vapor pressure in a type-2 situation can well be small enough to escape detection. For example, krypton exhibits no appreciable adsorption on sodium metal at 78 K and pressures up to saturation pressure.[4] This contrasts with the strong adsorption of Kr on graphite and other substrates at low pressure,[5–7] which seems to support the

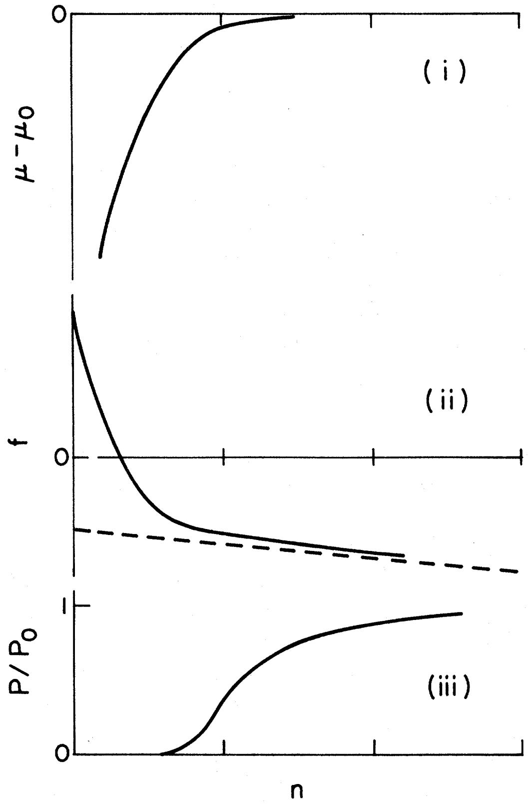

FIG. 1. Type-1 adsorption. (i) Variation of chemical potential μ with coverage n. μ_0 is the chemical potential for bulk phase. (ii) Free energy per molecule. (iii) Adsorption isotherm. In this type of adsorption all coverages are stable relative to bulk, i.e., film has uniform thickness at all n.

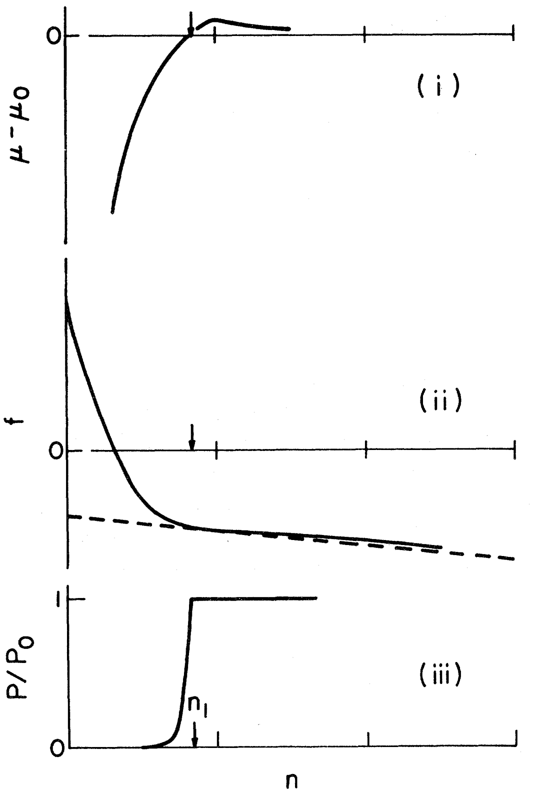

FIG. 2. Type-2 adsorption. (i) Chemical potential versus coverage. (ii) Free energy. The dashed line is the asymptotic slope of the bulk phase free energy at $n \rightarrow \infty$. In equilibrium there is no real curve between n_1 and infinite coverage: The curves for $\mu - \mu_0$ and f at $n > n_1$ represent the properties of a metastable film as uniform layers of intermediate thickness. (iii) Vapor pressure isotherm.

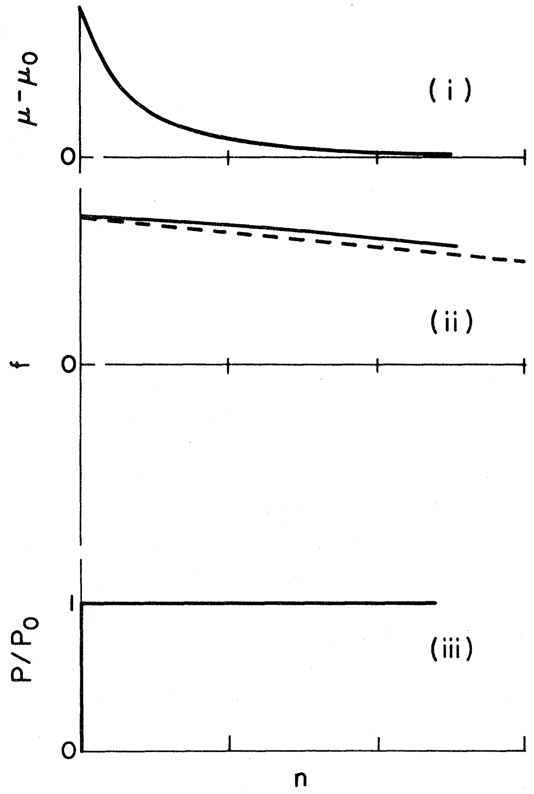

FIG. 3. Type-3 adsorption.

classification of Kr-Na as type 3. However, we now believe that the Kr-Na isotherm is actually an extreme case of type-2 adsorption, in which the coverage is below the limit of sensitivity in that experiment. (It is estimated that a coverage of up to several percent of a dense monolayer could have escaped detection.[8])

Although such adsorption is much weaker than on other substrates, it does not require abnormally low substrate attraction. Even if the coverage of the Kr-Na film just below saturation pressure is as low as one percent of maximum monolayer density, it would imply a density about 1.5×10^4 times that of the vapor. A Boltzmann factor of this magnitude at 78 K requires a substrate potential $\epsilon/k = 750$ K, about one-half of the graphite value.

It should be noted that, although there may be no real cases of type-3 adsorption, but only of extremely weak type 2, there can be a fairly sharp threshold between weak and strong type 2, due to the effect of adatom-adatom interactions. At temperatures below the critical temperature for monolayer condensation to a dense phase, the adatom-adatom interaction energy can add to the substrate binding. If the two-dimensional vapor density of the film due to substrate attraction alone can reach the saturation density of the dense monolayer phase, then the resulting condensation will add to the total binding. The enhancement can be quite significant in many cases: in the Kr-graphite system, for example, the total may be as much as twice that of the substrate alone.

(2) An earlier paper[2] distinguished two types, 2a and 2b, according to whether the bulk liquid formed beyond the maximum uniform film does or does not wet the surface with this film. The latter occurs if the cosine of the wetting angle computed from the classical Young-Dupré relation would have to be less than -1. The cited paper by Dzyaloshinskii *et al.*[3] estimates this quantity [see their Eq. (5.10)] and finds the cosine very close to $+1$, so that nonwetting would appear to be a very remote possibility.

However, this estimate assumes that n, the coverage for the thickest stable uniform film, is very large compared to a monolayer. (In their example[3] the thickness is taken as 5×10^{-5} cm.) The condition for the wetting angle is

$$\cos\theta=\frac{\gamma_{sv}-\gamma_{sl}}{\gamma_{lv}}\ , \tag{1}$$

where, as in our previous papers, the subscripts s, l, and v stand for the substrate, liquid, and vapor, respectively, and γ denotes surface tension. γ_{sv} includes the stable uniform layer and therefore can be written as $\gamma(n_1)$, where $\gamma(n)$ is the surface free energy of the substrate with a uniform adsorbed film of coverage n, which satisfies at constant temperature the thermodynamic identity

$$d\gamma=-n\,d\mu\ , \tag{2}$$

μ being the chemical potential per unit mass. Since $\gamma(n)$ must, for infinite n, approach the sum of the surface tensions between substrate and liquid, and between liquid and vapor, we have

$$\begin{aligned}\gamma(n)&=\int_n^\infty n\frac{d\mu}{dn}dn+\gamma_{sl}+\gamma_{lv}\\&=\int_n^\infty n\frac{d(\mu-\mu_0)}{dn}dn+\gamma_{sl}+\gamma_{lv}\ .\end{aligned} \tag{3}$$

Integrating by parts and setting $n=n_1$, the maximum coverage for uniform adsorption,

$$\begin{aligned}\gamma(n)=&-\int_{n_1}^\infty(\mu-\mu_0)dn+[n(\mu-\mu_0)]_{n_1}\\&+\gamma_{sl}+\gamma_{lv}\ ,\end{aligned} \tag{4}$$

where μ_0 is the chemical potential of saturated vapor. Since $\mu=\mu_0$ both in the bulk limit and at n_1, the second term cancels, and (1) becomes

$$1-\cos\theta=\frac{1}{\gamma_{lv}}\int_{n_1}^\infty(\mu-\mu_0)dn\ . \tag{5}$$

Here the integral is taken through an unstable region, since we assume type-2 behavior, in which films exceeding n_1 are unstable, with $\mu-\mu_0$ positive. If we assume, as in Ref. 3 that the deviation from bulk is dominated by a van der Waals type force, the integrand is A/n^3, with constant A, so

$$1-\cos\theta=A/2n_1^2\ . \tag{6}$$

The answer is therefore sensitive to n_1, i.e., to the thickness at which the force changes from repulsion to attraction, for which there is no exact theory. Taking this thickness to be 5×10^{-8} cm, but using otherwise the values chosen by Ref. 3, we would obtain about 1.5 for $1-\cos\theta$. Evidently a very modest change in the parameters could make $\cos\theta$ less than -1, so that there would be no wetting at all.

(3) Our third comment concerns the influence of curvature of the liquid-vapor interface. In type-2a adsorption, the transition from the homogeneous film to the drop wetting the surface will, on a microscopic scale, be continuous, and in this region the interface has a curvature which is concave towards the vapor. This reduces the chemical potential, as required to compensate the excess value (Fig. 2) for a thickness at which the film would be unstable.

To see the effect of this, consider the balance of forces on an element of surface of width dx, assuming the x direction to be along the substrate surface, and the normal to the liquid surface to lie in the xz plane. The surface tension γ_{lv} causes a surface stress. Its horizontal component is $\gamma_{lv}\cos\theta$. The net horizontal force on a surface element between x and $x+dx$ (and of unit width in the y direction) is

$$\frac{d}{dx}(\gamma_{lv}\cos\theta)dx\ .$$

There is also a pressure difference between the liquid film and the vapor, which gives rise to a force in the direction of the surface normal. This pressure difference can be related to the chemical potential. If we define the chemical potential of the system as μ_0 for a planar interface and μ when it is curved, the pressure difference across the surface is $(\mu-\mu_0)(\rho_L-\rho_v)$, where ρ_L and ρ_v are the densities in the film and the vapor. In typical situations $\rho_v<<\rho_L$, and we can neglect the vapor density and approximate the pressure difference by $(\mu-\mu_0)\rho_L$.

To obtain the horizontal component of this force, we multiply by $\sin\theta$, and the surface area of an element of projected area dx is $dx/\cos\theta$. The horizontal component of the normal force is therefore

$$(\mu-\mu_0)\rho_L\tan\theta=(\mu-\mu_0)\rho_L\frac{dz}{dx}\ .$$

As ρ_L denotes the film density at the interface, $\rho_L dz=dn$, so for equilibrium

$$\frac{d}{dx}(\gamma_{lv}\cos\theta)=-(\mu-\mu_0)\frac{dn}{dx}\ . \tag{7}$$

Integrating

$$\gamma_{lv}\cos\theta=-(F-n\,\mu_0)+\text{const}\ , \tag{8}$$

where F is the free energy per unit surface area, satisfying

$$\frac{dF}{dn}=\mu \ .$$

On the other hand, (2) can be written as

$$d\gamma_{sv}=\mu dn-d(n\mu)=dF-d(n\mu) \ ,$$

so that

$$\gamma_{sv}=F-n\mu_0 \ . \tag{9}$$

[Relation (9) was obtained in Ref. 2 by a rather roundabout argument.] Evaluating (8) for $n=n_1$, when $\theta=0$,

$$\gamma_{lv}=-\gamma_{sv}(n_1)+\text{const}$$

[note that at n_1 the chemical potential is μ_0, by assumption, so that we can use (9)] and the constant is seen to have the value $\gamma_{sv}(n_1)+\gamma_{lv}$. So, finally,

$$\gamma_{lv}\cos\theta=-(F-n\mu_0)+\gamma_{sv}(n_1)+\gamma_{lv} \ . \tag{10}$$

For large n, $F-n\mu_0=\gamma_{sl}+\gamma_{lv}$, so that (10) reduces to the usual condition for the wetting angle.

We may now ask how rapidly θ changes from 0 to its asymptotic value. The answer is contained in (8), and we have to ask how rapidly the right-hand side of (8) approaches its asymptotic value. If the deviation from the bulk value is due to forces of the van der Waals type, it varies as an inverse power of n, and will become small compared to its initial value when n is a multiple of n_1. Hence, on a macroscopic scale the change is discontinuous. Other forces tend to vary exponentially with distance, i.e., more rapidly than an inverse power.

On a large scale, the curvature of the surface of a drop adhering to the surface must eventually be convex towards the vapor, and this increases the chemical potential above the bulk value. (The discussion of this point in Ref. 1 was not correct.) On the face of it, it might appear that such a drop could not be stable in the presence of bulk liquid elsewhere.

This paradox is resolved by considering a finite amount of liquid present in addition to the uniform adsorbed layer. Let the mass of this be M. Far from the adsorbing surface (and in the absence of gravity) the equilibrium shape of this is a spherical drop of radius R, where

$$\frac{4\pi R^3}{3}=M \ .$$

A drop adhering to a plane substrate with wetting angle θ will form a spherical cap of radius R', where

$$\frac{\pi R'^3}{3}(2-3\cos\theta+\cos^3\theta)=M \ .$$

The value in parentheses in this expression is always less than 4, for θ less than 2π, and therefore $R'>R$. The curvature of the drop adhering to the surface is therefore less than that of the isolated drop and the former is the stable form.

It follows that the equilibrium configuration for liquid wetting a homogeneous surface is for all the liquid to form a single adherent drop. However, the differences in chemical potential involved here are minute, and therefore many small adherent drops may not coalesce into a single one in any reasonable time. Also a very slight heterogeneity of the substrate may result in many small droplets being more stable than a single large one.

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