Structure of surface layers and thin films of a dense simple liquid: weak-ordering region

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We investigate analytically the asymptotic behavior of a surface perturbation of the density profile of a liquid at large distances from the surface. A representation of the density of an ordered layer is obtained in the form of an aggregate of exponentially damped density waves. The reciprocal lattice and the correlation lengths of the layer structure are expressed in terms of experimentally obtained quantities. The predominant ordering, in the form of layers parallel to the surface, leads to oscillations of the free energy of a thin film as a function of its thickness. These oscillations determine the physics of the wetting of various surfaces by a dense liquid.

1. INTRODUCTION

The atomic structure of a liquid near phase boundaries is manifested in the properties of these phase boundaries and of thin films, and is investigated in experiments on wedging-out pressure,[1,2] on surface melting,[3] and on wetting.[4] Surface-layer structure was investigated also by computer simulation[5,6] and, finally, analytically for a number of models. In particular, an expression was obtained[7] for the density profile $n(\mathbf{r})$ of hard-sphere (HS) and hard-wall (HW) liquids by solving the Percus-Yevick (PY) equations for a mixture of HS having different radii, in the limit when the radius of the large spheres tends to infinity and their density to zero. The use of this solution, and also of a large number of data on the simulation of an HS-HW system had permitted development of a perturbation theory[5] for systems with real potentials. The most sophisticated variant of the theory[8] is in excellent agreement with the simulation, but no longer leads to analytic solutions.

An alternate approach for a liquid-gas interface was developed in Ref. 9. It is based on a representation of the system's free energy in the form of a functional of the liquid density (cf. Ref. 10, § 8.3), and its parameters are correlation functions of a massive liquid. A numerical investigation of a reasonable nonlocal model of this functional[11] yields good results. An analytic solution was obtained in Ref. 12, but only for a model in which the melt is represented by a sum of density waves with having the vectors of the reciprocal lattice of the crystal into which it crystallizes and on which it borders. The amplitudes of these waves are regarded as functions of the distance z from the wall, which vary slowly over distances on the order of interatomic. Accordingly, the nonlocality of the density of the free energy is taken into account by gradient terms, and this leads to an exponential decrease of the amplitudes into the interior of the liquid.[13] Such a law follows directly also from the "relay" mechanism—each succeeding atomic layer (counting from the surface) inherits a definite fraction of the ordering of the preceding one.

We present here a general solution of the problem of the structure and energy of the surface layer of a liquid; the solution is valid outside the atomic vicinity of the wall, i.e., at z exceeding several (in practice, one or two) atomic diameters a. In the region $z \approx a$ we use the PY approximation. The asymptotic form of the solution uses only the pair correlation function of the liquid, which is known from diffraction experiments and determines fully both the nonlocal quadratic functional of the density,[14] and the Ornstein-Zernike equation used here. Both methods lead to a representation of the near-surface density in the form of a superposition of a discrete set of waves (cf. Ref. 15) with characteristic wave vectors $\mathbf{k}_j$ determined by intrinsic short-range order of the liquid and by symmetry-group transformations that are absent in a system with a surface. These waves attenuate exponentially over correlation lengths $\xi_j = \xi(\mathbf{k}_j)$ that can be expressed in terms of the structure factor $G(k)$ of the liquid. Thus, any surface violating the translational symmetry along the z axis, excites in the liquid waves of smectic order $\exp(\pm ik_j z)\exp(-z/\xi_j)$, where k_j corresponds to the jth maximum of $G(k)$, and ξ_j is equal to the reciprocal half-width of this maximum.

Using next the PY solution for a HS-HW system and the density functional, we determine the amplitude of the waves and the energy density in them, obtain the structure term of the free energy of a thin film, investigate the influence of van der Waals forces, and obtain finally the conditions for wetting a solid surface.

2. EQUATIONS OF SURFACE-LAYER STRUCTURE AND ASYMPTOTIC SOLUTIONS

The Ornstein-Zernike relation (Ref. 10, p. 280)

$$h(\mathbf{r}_1, \mathbf{r}_2) = c(\mathbf{r}_1, \mathbf{r}_2) + n_0 \int c(\mathbf{r}_1, \mathbf{r}_3) h(\mathbf{r}_3, \mathbf{r}_2)\, d^3r_3 \qquad (1)$$

determines the direct correlation function $c(\mathbf{r}_1,\mathbf{r}_2)$ in terms of the complete one $h(\mathbf{r}_1,\mathbf{r}_2) \equiv n_2(\mathbf{r}_1,\mathbf{r}_2)/n_0^2 - 1$, where n_0 is the density of the uniform liquid, and n_2 is the two-particle density. In a homogeneous system we have $y(\mathbf{r}_1,\mathbf{r}_2) = y(|\mathbf{r}_1 - \mathbf{r}_2|)$, where $y = c, h$. Transforming

$$\tilde{y}(\mathbf{k}) = n_0 \int y(\mathbf{r}) e^{i\mathbf{kr}}\, d^3r = 4\pi k^{-1} n_0 \int_0^\infty y(r) \sin(kr)\, r\, dr, \qquad (2)$$

we solve (1) in the form

$$\tilde{c}(\mathbf{k}) = \tilde{h}(\mathbf{k})/[1 + \tilde{h}(\mathbf{k})] = 1 - G^{-1}(k). \qquad (3)$$

The structure factor $G(k)$, in the case of an ordinary dense liquid considered incompressible in hydrodynamics, is characterized (see Ref. 10, p. 318) by a high sharp peak at the point $k_1 = 5\pi/2a$ [at the triple point $G(k_1) \approx 3$], which re-

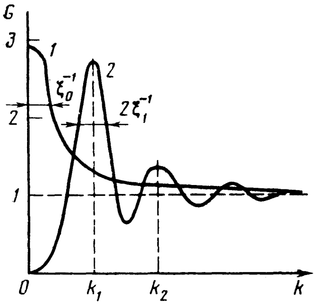

FIG. 1. Structure factor of simple liquid: 1—$T \approx T_c$; 2—$n0 \approx a^{-3}$.

flects spatial modulation of the short-range order, and a minimum at the point $k_0 = 0$: $G(0) = n_0 T\chi \sim 10^{-2}$, and χ is the compressibility (Fig. 1, curve 2). Predominating at the critical point, however, is a peak at zero, which corresponds to advanced fluctuations of the density (Fig. 1, curve 1).

For this density profile we can introduce a direct surface-liquid correlation function c_S (cf. Ref. 7) by means of the relation

$$\Delta n(\mathbf{r})/n_0 = c_S(\mathbf{r}) + n_0 \int c_S(\mathbf{r}) h(\mathbf{r}-\mathbf{r}_1)\, d^3 r_1, \qquad (4)$$

where h corresponds to the homogeneous state.

Introducing the function

$$y'(\varkappa, z) = n_0 \int y(\mathbf{r}) \exp[i(\varkappa_x x + \varkappa_y y)]\, dx\, dy, \qquad (5)$$

where $\varkappa$ is the wave vector in the plane of the surface, and $y = c_S, h, \Delta n$, we rewrite (4) in the form

$$\Delta n'(\varkappa, z) = c_S'(\varkappa, z) + \int_{-\infty}^{\infty} c_S'(\varkappa, z_1) h'(\varkappa, z - z_1)\, dz_1. \qquad (6)$$

The symmetry of c_S in the plane of the surface should coincide with the lowest of the symmetries of the boundary phases. Therefore $c_S'(\varkappa, z) \neq 0$ only for $\varkappa = 0$ in the case of a structureless substrate and for $\varkappa$ from the set $\{\mathbf{g}\}$ of the reciprocal lattice vectors of the crystalline surface. In the theory of liquids it is usually assumed[16] that as $r \to \infty$ we have $c(r) \approx -v(r)/T$, where v is the interparticle potential. In accord with the ideas of perturbation theory,[5,17] we assume

$$c_S(\mathbf{r}) = c_1(z - z_0) + V_S(\mathbf{r}), \qquad (7)$$

where c_1 is the modified PY solution[7] for c_S of the HS-HW system, and V_S is the summary potential of the substrate with the singular repulsive part subtracted. For the coordinate of the effective HW (Ref. 5) we assume $z_0 = 0$. Then $c_1(z) \neq 0$ only in the region of the wall ($z < 0$). Therefore, neglecting for the time being the weak power-law tail of V_S, we find that $c_S(z)$ differs from zero only near the surface itself, at $z < \mathbf{a}$. It follows hence that the asymptote n' differs from the asymptote h':

$$h'(\varkappa, z) = \int_{-\infty}^{\infty} \tilde{h}[(\varkappa, q)] e^{iqz}\, dq/2\pi = i \sum_{\operatorname{Im} q_0 > 0} e^{iq_0 z} \operatorname{res} \tilde{h}[(\varkappa, q_0)], \qquad (8)$$

since the integral in (2) converges regularly for the short-range function $c(r)$, so that $\tilde{c}$ is an analytic function of the complex k and the poles $\tilde{h}$ are simple.

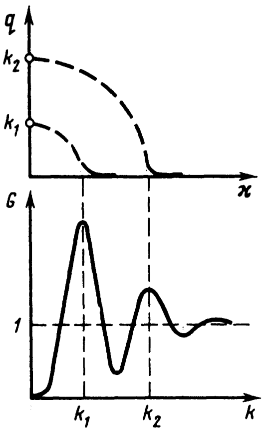

FIG. 2. Structure of solutions in k-space: points—l waves, dashed—m waves; solid curve—t waves.

According to (3), $q_0 = q + i/\xi$—the poles $\tilde{h}[\varkappa, q]$—are roots of the equation

$$\tilde{c}[(\varkappa^2 + q_0^2)^{1/2}] = 1. \qquad (9)$$

This equation can be obtained also by minimizing a quadratic functional that is valid in the asymptotic region (Ref. 10, § 8.3), viz.,

$$F(\{n\}) = \int \Delta n(\mathbf{r}) \left\{ \frac{T}{2} \left[\frac{\Delta n(\mathbf{r})}{n_0} - \int \Delta n(\mathbf{r}_1) c(\mathbf{r} - \mathbf{r}_1)\, d^3 r_1 \right] + V(\mathbf{r}) \right\} d^3 r. \qquad (10)$$

Indeed, by varying (10) in the absence of an external field ($V = 0$), we obtain an equation for Δn:

$$n_0 \int c(\mathbf{r} - \mathbf{r}_1) \Delta n(\mathbf{r}_1)\, d^3 r_1 = \Delta n(\mathbf{r}). \qquad (11)$$

The transformation (2) of this equation returns us to (9), i.e., the sought solution is a superposition of density waves with $\mathbf{k}$ such that $\tilde{c}(\mathbf{k}) = 1$. Being interested in weakly damped waves with small ξ^{-1}, we expand c in (9) in terms of this parameter and equate the imaginary and real parts:

$$\tilde{c}(k) - {}^1/_2(\xi k)^{-2}[q^2 d^2\tilde{c}/dk^2 + \varkappa^2 k^{-1} d\tilde{c}/dk] = 1, \qquad (12)$$

$$(\xi k)^{-1} q\, d\tilde{c}/dk = 0, \qquad (13)$$

where $k = (\varkappa^2 + q^2)^{1/2}$. Expressing $\tilde{c}$ in terms of G (13) with the aid of (3), we obtain three types of solutions of the system (12) and (13) (Fig. 2), i.e., three types of wave.

1) m wave (mixed)—smectic layers with normal $\mathbf{k}/k$:

$$q = \pm(k_i^2 - \varkappa^2)^{1/2}, \qquad \xi^2 = \xi_{mi}^2(\varkappa) = -\frac{d^2G/d\varkappa^2}{2G(k_i)} \frac{k_i^2 - \varkappa^2}{k_i^2}, \qquad (14)$$

k_i is the abscissa of the ith peak of G (Fig. 2).

2) A particular case of m waves: at $\varkappa = 0$ we have l waves (longitudinal)—smectic layers parallel to the surface:

$$q = \pm k_i, \quad \varkappa = 0, \qquad \xi^2 = \xi_i^2 \equiv -[2G(k_i)]^{-1} d^2G/dk^2|_{k=k_i}, \qquad (15)$$

ξ_i is the reciprocal half width of the ith peak; only these waves contribute to the density profile $n(z) = \int n(r)\, dx\, dy/S$ (S is the surface area) that is presented in papers on modeling.

3) *t* waves ("transverse")—two-dimensional order in the surface plane:

$$\begin{aligned} &\varkappa\approx k_i:\quad q_t\approx(k_i/\xi_i)^{1/2},\qquad \xi_t\approx(\xi_i/k_i)^{1/2};\\ &\varkappa>k_i:\quad q=k_i/\xi_i(\varkappa^2-k_i^2)^{1/2},\qquad \xi=(\varkappa^2-k_i^2)^{1/2}. \end{aligned} \tag{16}$$

Substitution of (14)–(16) in (8) yields the asymptote h':

$$h'(\varkappa,z)=\begin{cases} \dfrac{G(k_1)}{\xi_1}\dfrac{k_1}{(k_1^2-\varkappa^2)^{1/2}}\cos(k,z)\exp\left[-\dfrac{k_1|z|}{\xi_1(k_1^2-\varkappa^2)^{1/2}}\right], & 0\leqslant\varkappa\leqslant k_1,\\ [G(\varkappa)/2\xi_t(\varkappa)]\exp[-|z|/\xi_t(\varkappa)], & k_1<\varkappa<k_1'. \end{cases} \tag{17}$$

The asymptote of the radial distribution function of a bulk liquid is obtained analogously[18]

$$h(r)\propto r^{-1}\sin(k_1r)\exp(-r/\xi_1).$$

Finally, substitution of (17) in (4) expresses the complex amplitude of the wave Δn_k in terms of c_S. Namely, for an *l* wave we have

$$\Delta n_l=(n_{l+}e^{ik_1z}+n_{l-}e^{-ik_1z})e^{-z/\xi_1}=2|n_{l\pm}|\cos(k_1z+\varphi_1)e^{-z/\xi_1}, \tag{18}$$

$$n_{l+}=n_{l-}^{*}=\frac{n_0G(k_1)}{2\xi_1S}\int c_S(\mathbf{r})\exp[(-ik_1+\xi_1^{-1})z]\times d^3r\equiv n_0G(k_1)c_{Sl\pm}, \tag{19}$$

$$c_{l+}=\dot{c}_{l-}=\frac{1}{2S\xi_1}\int c_S(\mathbf{r})\exp[(-ik_1+\xi_1^{-1})z]d^3r,$$

$$\varphi_1=\arg c_{Sl+}=-\arg c_{Sl-}. \tag{20}$$

3. BOUNDARY LAYER OF LIQUID

1. Structure of boundary layer. We note first of all that, naturally, expansion of $\tilde{c}(k)$ in powers of $(k\xi)^{-1}$ is equivalent to representing a nonlocal correlation interaction in the form of an expansion in powers of the squares of the density gradients $(dn_\mathbf{k}/dz)^2$. Namely, an inverse Fourier transform of (12) with respect to the imaginary part of the wave vector, with allowance for (13), yields an equation that can be obtained by variation of the functional

$$F=\frac{T}{2}\int\left\{\sum_\mathbf{k}|n_\mathbf{k}(z)|^2[1-\tilde{c}(\mathbf{k})]-\frac{1}{2}\sum_\mathbf{k}\frac{\partial^2\tilde{c}(\mathbf{k})}{\partial k_z^2}\left|\frac{dn_\mathbf{k}(z)}{dz}\right|^2\right\}dz, \tag{21}$$

where the set **k** is defined by the condition (13). The single density wave obtained correspondingly in Ref. 13 by a gauge expansion near a structureless wall is equivalent to our *l* wave (16). Ref. 13, however, contains an algebraic error in the calculation of ξ_1.

Minimizing (10) at $V\neq0$, it is easy to show with allowance for (3) that G has the meaning of linear susceptibility—the classical Green's function of a liquid, and Eq. (9) determines its poles, i.e., the elementary excitations. Clearly, the lowest to attenuate are the waves corresponding to poles in the vicinity of the principal susceptibility peaks at real k, i.e., the soft modes easiest to excite.

If the density (and temperature) of the liquid are close to critical, $G(k)$ has a single peak $k_0=0$. Substitution of k_0 in (15) and (16) yields $\mathbf{k}=0$, i.e., the density of the rarefied liquid (fluid) decreases monotonically as the distance from the wall becomes of the order of the characteristic correlation length ξ_0 which is equal to the reciprocal of the half width of the $G(0)$ peak. The inhomogeneous system is described in this case by the functional (21) with a single gradient term for $k=0$. This functional describes a transition into a state of total wetting.[19,4]

Predominant in a dense liquid is a susceptibility peak at finite $k_1=5\pi/2a$, and at the point k_0 the function G has a minimum (in this sense a liquid is analogous to paramagnet with ferromagnetic short-range order in the critical region, and with antiferromagnetic short-range order at high densities[13]). Therefore the monotonically decreasing condensation or rarefaction near the walls becomes unstable in the asymptotic zone—the coefficient of d^2n_0/dz^2 in (21) is proportional to $-G''(0)$ and is consequently negative (this circumstance was omitted in Ref. 13).

Soft modes are waves of smectic order $\Delta n\propto\cos(\mathbf{kr}+\varphi)$ with $|\mathbf{k}|=k_1$. These modes are constantly present in a bulk liquid at thermal equilibrium, but the arbitrariness of the phase φ in the **k** direction causes them to cancel out. A surface, on the other hand, fixes both the phase and the direction of **k** and "displays" the soft mode.

The first $G(k)$ for a Lennard-Jones potential[20] and for melts of similar metals is well described by the analytic solution $c_{\rm PY}$ of a liquid of hard-spheres[10] with suitably chosen[17] diameters. The universal dependence of the characteristic damping length ξ_1 of the density waves on the average liquid density n_0, obtained by numerically solving (9), is shown in Fig. 3. The density at the triple point corresponds to $n_0a^3\approx0.85$–0.9 (Refs. 20 and 6), i.e., $\xi_1\approx(1.35$–$1.55)a$ (≈5 Å for lead). It follows hence that $\xi_1k_1\approx10\gg1$, thereby justifying the expansion (12), (13) and also the gradient expansion of the free-energy functional. The validity of the expansion is confirmed also by the fact that the wave damping length ξ_1, calculated using (15), differs from the values in Fig. 3 by less than 10%. An estimate of the damping length ξ_2 of the second harmonic of an *l* wave using the $G(k)$ curves from, e.g., Refs. 20, 21, and p. 318 of Ref. 10, yields $\xi_2=\xi_1/4$. For *t* waves with $\varkappa\approx k_1$ we get $\xi_t\approx\xi_1/3$ from (16).

The asymptote of the surface density perturbation, as well as of the radial distribution function, is determined primarily by the *l* wave (18) which is due to the breaking, by the surface, of the translational symmetry along the z axis. On a crystal surface, the symmetry is broken also in its plane, so that *m* and *t* waves are observed on the plane, with $\varkappa$ from the set $\{\mathbf{g}\}$.

To complete the solution we use a suitably renormalized[17] correlation function for hard spheres near a hard

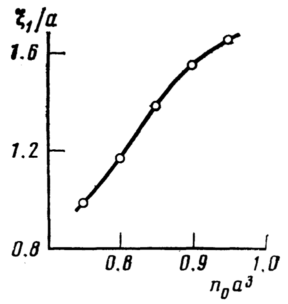

FIG. 3. Correlation length of l waves vs density.

well[7]; we substitute $c_S = c_1$ from Ref. 7 [see Eq. (7)] in (20) and (19) and obtain the amplitudes $n_{l\pm}$ for l waves. The amplitudes of the other wave follow similarly from (17) and (4). A numerical analysis (the analytic expressions are unwieldy) has shown that when n_0a^3 increases from 0.75 to 0.90, the ratio $|n_{l\pm}|/n_0$ increases respectively from 0.7 to 0.8. At the point of the first and deepest minimum of $n(z)$ with $z \approx a$, expression (18) yields

$$\Delta n_l/n_0 \approx 2|n_{l\pm}|e^{-a/\xi_1} \approx |n_{l\pm}|/n_0.$$

The proximity of these last numbers to unity shows the high degree of modulation of the density of the liquid near a solid wall—it is only 20–30% lower than that of the crystal surface. It is this modulation that causes the periodic dependence, discussed in Sec. 4 below, of the energy of a thin film on its thickness, and the discrete character of the wetting effects (Sec. 6).

We analyze now the results of simulation of the structure of the melt of a Lennard-Jones crystal near the faces (111), (110), and (100). The faces (111) and (100) excite well-pronounced l waves, and as the distance from (100) increases we get the theoretically predicted restructuring of the period of the oscillations, from the interplanar distance d_{100} imposed by the crystal, to the natural wavelength $2\pi/k_1 \approx d_{111}$ of a close-packed liquid. The l wave is not pronounced on the (110) face; this is due, in our opinion, to the strong disparity between $d_{100} = (3/8)^{1/2}d_{111} \approx 0.6d_{111}$ and the period of the l wave, and also to the advanced fluctuations of the surface roughnesses (see below).

Of greater importance for the structure of the liquid perturbation at the (110) face of an m wave with

$$\varkappa = \pm(0,\ 0,\ 2\pi), \qquad \xi_m = \xi_1(k^2-\varkappa^2)^{1/2}/k_1 \approx (2/3)^{1/2}\xi_1 \approx 0.8\xi_1,$$

which is a continuation of two systems of (111) planes. Actually, m waves with $\xi \approx \xi_1$ are produced on planes with large Miller indices, where $\{\mathbf{g}\}$ includes $|\mathbf{g}| \ll a^{-1}$. On the faces (111) and (100), the two-dimensional crystalline order carried by the t waves attenuates much more rapidly than the smectic l order.

2. Influence of surface perturbations. In accordance with the foregoing, density waves should appear whenever translational invariance is violated, i.e., also on a liquid-gas boundary. It is indeed observed in models,[22] if one considers instantaneous photographs of a structure not averaged over areas along the surface which are large in atomic scale. In opposite cases, the density waves inside the liquid should obviously be smeared out by displacements of the surface when capillary waves propagate over it. If the effective smearing of the surface is equal to $\Delta \approx [(T/\alpha)\ln(\alpha a/mg)]^{1/2}$ (Ref. 23), the observed amplitude n_l of the density waves in the liquid decreases to $n_l\exp[-(k_1\Delta)^2]$. Here α is the free-surface energy, m the mass of the liquid particle, and g the acceleration due to gravity. For water at $T \approx 300$ K we have $T \approx 300$ K, $\Delta \approx 14$ Å, $k_1 \approx 2$ Å^{-1} and $n_l \ll n_0$, i.e., a layered structure is observed only at frequencies much higher than capillary. Nonetheless, this structure does manifest itself in thin films, where the interaction with the other surface suppresses the capillary fluctuations and exerts the decisive influence on the physics of the wetting (Sec. 5).

A similar smearing of density waves is possible also in a liquid bordering on an atomically rough crystal boundary (provided, of course, that the distance between the crystal grids parallel to the surface differ noticeably from the wavelength $2\pi/k_l$ in the liquid). This is apparently the situation on the (110) face of a Lennard-Jones system, where the observed propagation, into the interior of the melt, of oscillations with period d_{110} is a manifestation of the fluctuation smearing $\sim\exp[-(nd/\Delta)^2/2]$, i.e., of the nonzero probability of successive elementary steps on the surface.[24,25] On the contrary, on the atomically smooth sections of the surface, in view of the discrete character of the atomic structure of the crystal, we have $\Delta \ll a$ and the density waves in the liquid should be distinctly pronounced. Steps of other inhomogeneities, with distances considerably greater than $2\pi/k_1$ between them, lead to a block structure of the surface layer, but does not upset the order over any smooth terrace.

3. It is easily seen that a slowly damped l wave carries with it a perturbation, proportional to $(\Delta n_l)^2$, of the average scalar properties of the system. Therefore, for example, a surface perturbation of the average energy of the particles, or the monotonic component of the density perturbation, decreases like $\exp(-2z/\xi_1)$ in accordance with the simulation results.[6] On the other hand, substitution in (10) of a density wave that satisfies (11) yields zero, i.e., the free-energy density is $o[(\Delta n_l)^2]$ and is concentrated in a narrow surface zone.

4. FREE ENERGY OF A THIN FILM

The arguments in Sec. 3.3. show that any scalar order parameter that characterizes a surface perturbation has a correlation length $\xi = \xi_1/2$. Constructing a functional of the Ginzburg-Landau type for such an order parameter, we obtain[19,4] a monotonic dimensional free-energy increment proportional to $\exp(-2H/\xi_1)$, where H is the film thickness. There exists, however, a stronger interaction mechanism between the film boundary surfaces, via density waves. Indeed, the interaction between an l wave excited by the surface located at $z = 0$ and the field w of the surface located at $z = 0$ is of the form

$$\int_0^\infty w(z)\exp[(ik_1-\xi_1^{-1})(H-z)]dz \propto \exp[(ik_1-1/\xi_1)H].$$

Summing over the four l waves in the film, we obtain a free-energy shift (per unit area) equal to

$$\Delta f_l = \varepsilon\cos(k_1H+\varphi_2)\exp(-H/\xi_1)/a^2. \qquad (22)$$

This law is proved in the Appendix. The amplitude ε will be estimated below. A t or m wave in which $\varkappa \neq 0$ [see (14), (15)] can interact only with a $\varkappa$ harmonic of the field w. But w, just as c_S [see (23) below] has nonzero harmonics for $\varkappa$ from $\{g\}$ of the given surface. Coincidence of two crystal meshes in the laboratory frame, however, is impossible: an arbitrarily small misorientation of even two identical crystals leads to incoherence. There are therefore no dimensional corrections proportional to $\exp(-H/\xi_{t,m})$.

We estimate now the amplitude (22) of the oscillations of the film energy as a function of the thickness. Note that (4) can be formally obtained from (10) by putting $\hat{V} = -Tc_S$, since the operator that is the inverse of $\hat{1} - \hat{c}$ is $\hat{G} = \hat{1} + \hat{h}$ [see (3), where the unit operator $\hat{1}$ is $\delta(\mathbf{r}_1,\mathbf{r}_2)$ in the direct-space interaction. In the case of a short-range c_S at thicknesses so large that the c_S action zones do not overlap, the film can be satisfactorily described by Eq. (10) with

$$V=-T\sum_{\varkappa=g_1,g_2}[c_{S1}'(\varkappa,z)+c_{S2}'(\varkappa,H-z)]. \tag{23}$$

Then

$$\Delta f_1=-Tn_0\int'\sum_{\varkappa=g_1,g_2}c_{S1}'(\varkappa,z_1)c_{S2}'(\varkappa,z_2)h^0(\varkappa,H-z_1-z_2)\,dz_1\,dz_2. \tag{24}$$

Substituting (17) and (20) in (24) we get

$$\Delta f=\Delta f_l=-4Tn_0G(k_1)\xi_1\,\mathrm{Re}\,[\exp(ik_1H)c_{1l+}c_{2l+}]\exp(-H/\xi_1). \tag{25}$$

From this and from (19) we get an estimate for ε in (22) at $n_0 \sim a^{-3}$:

$$\varepsilon\approx 4TG^{-1}(k_1)(\xi_1/a)|n_{1l+}||n_{2l+}|/n_0^2. \tag{26a}$$

The estimates made for $|n_l|/n_0$ yield $\varepsilon \approx (2-3)T$.

Free-energy oscillations were observed on films of the large quasispherical molecule liquids CCl_4, cyclohexane, and OMCTS (octamethylcyclotetrasiloxane) at $T \approx 20°$ C.[2,26]. Within the limits of experimental error, they are described by (22) with $k_1 \approx 2\pi/a$, where a is estimated from independent (say, crystallographic) data, $\xi_1 k_1 \approx (1.1-1.4)\cdot 2\pi$ and $\varepsilon \approx (0.5-2.0)T$ (since $\Delta f_l \propto \exp(-H/\xi_1)$, the value of ε is strongly influenced by errors in the measurement of the absolute value of H). Simulation of a Lennard-Jones liquid with $n_0 = 0.59$ and $T = 1.1$ (in Lennard-Jones units) between HW with strong attraction[27] also yields $\Delta f_l(H)$, which is well described by Eq. (22) with the parameters $k_1 = 6.45$ and $\xi_1 = 0.72$ obtained by analysis of $G(k,n_0,T)$ (Ref. 20) and $\varepsilon \approx \varepsilon_{\text{theor}}/2$, where $\varepsilon_{\text{theor}}$ is given by (26) with n_l estimated from the solitary-boundary profile reported in Ref. 27. Thus the $\Delta f_l(H)$ dependence (22) agrees with experiment within the limits of experimental error. The linear model (10), (25) of the film overestimates ε by approximately a factor of 2. An alternate model, which permits a determination of ε, was developed in Ref. 28.

5. INFLUENCE OF LONG-RANGE FORCES

The influence of van der Waals forces $v_{VW}(r) \propto r^{-6}$ can be taken into account by perturbation theory,[17] by substituting in (10)

$$V=\int v_{VW}(\mathbf{r}-\mathbf{r}')\Delta n^{(0)}(\mathbf{r}')\,d^3r' \tag{27}$$

where $\Delta n^{(0)}(\mathbf{r}')$ is obtained by minimizing (10) at $v_{VW} = 0$. For large z this field can be represented by the series

$$V_S(z)=\sum_{m=3}^{\infty}u_m(a/z)^m, \tag{28}$$

where the coefficient u_3 is proportional to the difference between the polarizabilities of the liquid and the boundary phase,

$$u_m \sim \int_0^{\infty}\Delta n(z)z^{n-4}\,dz, \qquad n\geqslant 4$$

(the harmonics $u_g \exp[i(g_x x + g_y y)]$ of the field that varies along the crystal surface attenuate like $\exp(-|g|z)$). The leading term of (27) produces a monotonic compression (rarefaction):

$$\Delta n_0=-[G(0)n_0u_3/T](a/z)^3=-u_3n_0^2\chi(a/z)^3. \tag{29}$$

Since $G(0) \sim 10^{-2}$, the amplitude $\Delta n_l \gg \Delta n_0$ at $z \lesssim 10a$. On the other hand, the interaction of the field V_S produced by one surface with the matter of the opposite boundary phase produces a classical size-effect correction[1,2,4]

$$\Delta f_{VW}=A/12\pi H^2, \tag{30}$$

where the Hamaker constant is $A \approx \pm 10^{-13}$ erg for a liquid on a foreign substrate and can be an order of magnitude smaller for liquid-gas phases in the crystal-melt critical region.

6. PHASE EQUILIBRIUM OF A WETTING HEAVY-LIQUID FILM

Consider the boundary S of a crystal (c) with its own vapor (or vacuum) or of an arbitrary wall with gas (g). It is known that a thin film of the liquid-like state (l) can exist on the surface, i.e., surface melting of the crystal[3] or adsorption of liquid from the gas.[4] The question is: will the film remain finite when the vapor pressure approaches the equilibrium value over the bulk liquid (the difference of the chemical potentials of the liquid and of the gas $\Delta\mu = \mu_l - \mu_g \to 0$ above), or will it grow to form a macroscopic layer that wets the surface completely. This question was investigated in detail recently[19,4] for a liquid-gas system near the critical temperature, i.e., for slow monotonic functions $n(z)$ (Sec. 3.1). It was shown that when the temperature is raised along the equilibrium line ($\Delta\mu = 0$) and a certain point $T_W < T_c$ is reached, a phase transition from incomplete to complete wetting takes place and can be either jumplike (of first order), i.e., $H(T = T_W - 0, \Delta\mu = +0) < \infty$, or continuous. The influence of oscillatory effects, which determine the structure of a liquid at high densities, on the wetting was hardly discussed.

In the absence of surface fluctuations, the equilibrium thickness of the film H as $\Delta\mu \to +0$ is determined by the minimum of the free energy $\Delta f(H) = \Delta f_l(H) + \Delta f_m(H)$ (Fig. 4), where the oscillatory component Δf_l contains (22) and also, for liquid metals, a term connected with the Friedel oscillations of the electron density.[29] The monotonic component Δf_m is made up of a structural ($\propto \exp(-2H/\xi_1)$), a van der Waals (30), and a phonon ($-0.024\,T/H^2$, Ref. 30) terms. The latter is connected with the correlations of the wave motion of the liquid. Our estimates of ε in (22), experiment,[2,26] and simulation[27] show that at $H \lesssim 5a$ the amplitude Δf_l exceeds $|\Delta f_m|$ (Fig. 4). The minimum value of Δf in a

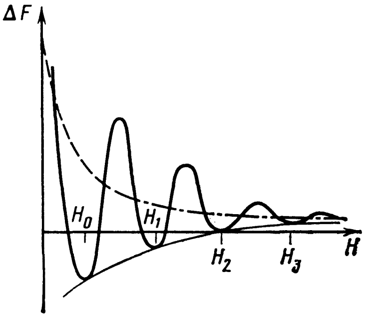

FIG. 4. Free energy of thin film of simple liquid: solid envelope $\propto \exp(-H/\xi_1)$; dashed curve—$\propto \exp(-2H/\xi_1)$; dash-dot curve—$\propto H^{-2}$.

dense liquid is consequently negative and is reached at $H = H_1 \sim a$ (Fig. 4). A film with $H = H_1$ wets a surface better than a bulk liquid ($H = \infty$), i.e., the wetting is incomplete. Under arbitrary (nonequilibrium) conditions the system is in one of the local minima of Δf at the points $H = H_j$ (Fig. 4). The film should therefore become thicker (thinner) via first-order transitions $H_j \leftrightarrow H_{j+1}$ and by overcoming appreciable barriers. Such transitions (layering), typical of growth of epitaxial films[24] by the Stransky-Krastanov mechanism, were observed in adsorption of ethylene by graphite.

The picture drawn above can change substantially if account is taken of the fluctuations of the film thickness $H(x, y)$, which are qualitatively described by the Hamiltonian[32]

$$F(\{H\}) = \int \left[\frac{\alpha}{2} (\nabla H)^2 + \Delta f(H) \right] dx\, dy, \qquad (31)$$

where $\alpha = \alpha_{\mathrm{lg}}$ in the case of adsorption (α_{lg} is the surface energy of the liquid-gas interface). At $T \ll \alpha a^2$ in a uniform periodic potential $\Delta f = 2Ty_0 \cos(k_1 H)$ the surface is in an atomically smooth state[33]: the order parameter is

$$\eta = [\lim_{x,y\to\infty} \langle [H(0,0) - H(x,y)]^2 \rangle]^{-1} > 0.$$

At $T = T_R = \alpha a^2 \psi(y_0) (\psi \sim 1, \psi(0) > 0)$, a second-order transition into a rough state takes place: as $T \to T_R - 0$ the parameter $\eta \to 0$, and as $T \to T_R + 0$ the correlation length in the surface plane $\xi_{\parallel} \to \infty$ ($\xi_{\parallel}$ has the meaning of the dimension of the regions with constant $H \approx H_j$). Clearly, in a real potential relief $\Delta f = \Delta f_l + \Delta f_m$ the lines of the $H_j \leftrightarrow H_{j+1}$ transitions terminate at the critical points T_{Rj} (cf. Ref. 34), defined implicitly by an equation such as

$$T_{Rj} = \alpha a^2 \psi \{\Delta f_l [(H_j + H_{j+1})/2]/T_{Rj}\}.$$

At $T \lesssim T_{Rj} \sim \alpha a^2$ the length $\xi_{\parallel} \gg 1$ and it is possible to consider independently capillary waves that do not take the sourface out of the jth potential well. These waves raise the free energy of the jth state: in the quasiharmonic approximation we have

$$\Delta f_j \to \Delta f_m(H_j) + \Delta f_l(H_j) \exp[(-k_1\Delta)^2],$$
$$\Delta_j^2 \approx (T/\alpha) \ln[1 + \mathrm{const}\cdot\alpha/|\Delta f_l(H_j)|]$$

(in this case, the boundary is pinned not by gravitation but by the considerably stronger field Δf_l). At $T \ll \alpha a^2$ the smearing $\Delta \ll a$ and the fluctuations are negligible. A rising temperature, however increases Δ and at $\Delta f_m > 0$ there exists a temperature T_W such that all $\Delta f(H_j) \geqslant 0$, i.e., a thick film ($H \to \infty$ as $\Delta\mu \to +0$) is favored. A first-order phase transition (cf. Ref. 4) takes place thus into a total-wetting state. This reasoning is valid, however, only if $T_W \ll T_c$; if, on the other hand, $T \to T_c$, we have $\Delta f_l \to 0$ by virtue of the decrease of ξ_1 and $G(k_1)$, and the degree of wetting is controlled by monotonic condensation or rarefaction of the fluid near the walls, and by the van der Waals[4] and phonon[30] components of the free energy.

Analysis of the surface melting is made complicated by the nonequivalence of the different positions of the crystal-melt surface; this can be taken into account[25,33] by adding to (31) with $\alpha = \alpha_{\mathrm{cl}}$ (one can neglect the fluctuations of the melt-gas surface in the analysis of surface melting of tight-binding substances, by virtue of $\alpha_{\mathrm{lg}} \gg T/a^2$) a periodic potential of the type $U(z_0) = U_0 \cos(2\pi z_0/d)$, where d is the corresponding distance between the planes. Application of U leads to a greater variety of phase diagrams. It is clear nonetheless that at large $\alpha_{\mathrm{cg}} a^2/T$ the fluctuations are suppressed by the steepness of the potential wells, and surface melting reduces to formation of a monoatomic quasiliquid film with atomically smooth surfaces. According to simulation data[35] this situation obtains on the (111) face of Si, in agreement with the observed incomplete wetting of the (111) faces of Si and Ge by bulky-melt droplets.[36] It is possible to interpret within the framework of this "incomplete" surface melting also the data on the disordering of singular surfaces of a number of metals (see Ref. 37). If, however, α_{cg} a^2/T is small, the advanced roughness fluctuations decrease both Δf_l and U. As a result, the dimensional correction to the free energy of the film becomes a monotonically decreasing function of its thickness, and infinite thickening of the film becomes favored. The observation of such a "complete" surface melting on the (110) face of Pb (Ref. 38) agrees with our analysis of a fcc crystal-melt (110) face. Thus, complete surface melting of simple substances is closely connected with roughness fluctuations of the crystal-melt surface, although it is a phenomenon quite different from roughness. This circumstance imposes particular requirements on the equilibrium of the simulation of surface melting. We emphasize that the foregoing conclusion pertains only to simple surfaces: complete surface melting (connected apparently with effects of liquid-crystal character) was observed on the basal face of diphenyl[39] that remained atomically smooth in contact with the melt.

A special case is that of surface melting on an interface with vacuum (cf. Ref. 38) or with a foreign substrate when the crystal-melt surface is atomically smooth. In this case the film thickness takes on only discrete values corresponding to an integer number of molten planes of the crystal. At close values of d and $2\pi/k_1$ [fcc (111)] all these values can land in the region $\Delta f > 0$ (Fig. 4) and the surface melting can be complete.

Note also that the existence of a smectic l structure on a liquid-gas surface (Sec. 3.2) is confirmed by observation of wetting of interfaces of an isotropic liquid with a gas and of a nematic with a gas by a smectic-phase layer.[40]

7. CONCLUSION

Equations of the Ornstein-Zernike type and a quadratic functional of the free energy permit an accurate description of the asymptotic structure of a liquid near a crystal (and, in general, a potential-relief) surface. The use of the solutions for a hard-sphere liquid near a smooth wall yields also estimates of the amplitudes of density waves exponentially damped in the interior of a liquid. Altogether, three types of wave turn out to be possible in dense liquids: longitudinal (smectic layers parallel to the wall), mixed (layers at angles to the wall), and transverse. The type of wave is determined by the reciprocal-lattice vector of the wall. Longitudinal waves are excited also by a structureless smooth surface. The characteristic depth of penetration of the wave into the liquid depends on the type of wave and on the length of the liquid's long-range order, which determines the liquid's structure factor measured in diffraction experiments.

The wave penetration depth depends strongly also on the fluctuations of the boundary: it is considerably smaller near atomically rough surfaces than near smooth ones. Similarly, capillary waves on a liquid-gas interface smooth out the inevitable density waves that oscillate together with this interface.

The described crystal-like ordering of the boundary layers of a simple liquid is responsible for the periodic dependence of the free energy of thin films on their thickness and for the oscillations of the wedging-out pressure. Finally, the discrete character of the same ordering determines the features of wetting of solid surfaces by liquids.

All the phenomena considered can, naturally, be greatly altered by electrostatic effects in electrolytes and by geometric effects in liquids made up of nonspherical molecules.

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APPENDIX

In the interior of the film, the density perturbation constitutes an aggregate of four l waves:

$$\Delta n(\mathbf{r})=\sum_{\beta,\nu=\pm} n(\beta,\nu)\exp[(\beta ik_1+\nu\xi_1^{-1})z] \tag{A.1}$$

with amplitudes $n(\beta,\nu)$, where the indices β and ν determine the directions of the propagation and damping of the wave, respectively. The contribution of the jth ($j=1,2$) near-surface zone to the free energy f_j can be represented as the function

$$f_j[n_j(+,+),n_j(+,-),n_j(-,+),n_j(-,-)],$$

where the n_j are defined in the jth reference frame (i.e., are reckoned from the jth surface). The quantities n_1 and n_2 are connected by the transformation

$$n_1(\beta,\nu)=n_2(-\beta,-\nu)\exp[-(i\beta k_1+\nu\xi_1^{-1})H]. \tag{A.2}$$

On a solitary surface j there are excited only damped waves, therefore the free surface energy α_j is determined by minimizing f_j at $n_j(\beta,+)=0$:

$$\alpha_j=f_j[n_j^{(0)}(+,-),n_j^{(0)}(-,-),0,0],$$

where $n_j^{(0)}$ is the equilibrium value of the amplitude. At small $\exp(-H/\xi_1)$ the coefficients $n_j(\beta,+)$ and the deviations $\delta n_j(\beta,-)=n_j(\beta,-)-n_j^{(0)}(\beta,-)$ are small and proportional to $\exp(-H/\xi_1)$. The energy f_j contains only corrections quadratic in δn_j, since $\partial f_j/\partial n_j(\beta,-)=0$ at $n_j(\beta,-)=n_j^{(0)}$. On the other hand the derivative $\partial f_j/\partial n_j(\beta,+)=w_j(\beta)\neq 0$ determines in the general case the surface field $w_j(\beta)$ that is conjugate to $n_j(\beta,+)$, and the interaction of the latter with the field leads to a correction linear in $\exp(-H/\xi_1)$:

$$\Delta f_l=\exp\left(-\frac{H}{\xi_1}\right)\sum_{\beta=\pm}[w_1(-\beta)n_2^{(0)}(\beta,-)+w_2(-\beta)n_1^{(0)}(\beta,-)]\exp(i\beta k_1H), \tag{A.3}$$

which is transformed into (22).

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