Journal of Statistical Physics, Vol. 47, Nos. 5/6, 1987

Some Aspects of the Wetting Transition[1]

J. K. Percus[1]

Received February 20, 1987

The wetting of an attractive planar wall by liquid at liquid–gas coexistence is investigated from a microscopic point of view. A model for interface detachment due to thermal fluctuations is first worked out. An empirical framework for distinguishing between first-order and continuous wetting transitions is then set up, and quantified by the introduction of the van der Waals mean field model. This is solved for strong, short-range and weak, long-range forces. The role of fluctuations is reconsidered, and the nature of the required corrections examined, both for wall–fluid and fluid–fluid interfaces.

KEY WORDS: Wetting transition; capillary waves; mean field model; nonuniform fluid.

1. INTRODUCTION

The study of macroscopic inhomogeneities of classical fluids in thermal equilibrium—e.g., under the action of a gravitational field—is anicent and not terribly interesting: local thermodynamics in the form

$$\mu - u(r) = \mu_T(n(r)) \tag{1.1}$$

suffices, or its Archimedean version

$$n(r)\,\nabla u(r) + \nabla P_T(n(r)) = 0 \tag{1.2}$$

Here $u(r)$ is the external potential, $n(r)$ is the fluid density, and $\mu_T(n)$ and $P_T(n)$ denote the thermodynamic chemical potential and pressure functions, respectively. Microscopic inhomogeneities, analyzable in detail

---

This paper was presented at the conference on the Statistical Mechanics of Phase Transitions—Mathematical and Physical Aspects, Třeboň, Czechoslovakia, September 1–6, 1986.

[1] Courant Institute of Mathematical Sciences and Physics Department, New York University, New York, New York 10012.

0022-4715/87/0600-0801$05.00/0

only by difficult experiments or computer simulations, are a different story. There are two major regions of interest: externally imposed inhomogeneities due, e.g., to a rigid boundary substrate, and internally maintained inhomogeneity at a two-phase interface. A fair amount of recent effort (see, e.g., Refs. 1–7) has been devoted to situations in which the two are in some sense in competition, and these will form the subject of the present work.

The phenomenon of one-component wetting (we will not discuss mixtures) is readily described in classical fashion (see Fig. 1). A liquid (L) drop which *partially wets* a bounding substrate (S) has its configuration within the gas (G) environment determined by the contact angle θ, satisfying the mechanical equilibrium condition of vanishing tangential force:

$$\sigma_{sg} - \sigma_{sl} = \sigma_{lg} \cos \theta \tag{1.3}$$

where the σ's are the respective surface tensions or works of formation of unit interfacial area. One can then travel parametrically in two directions to prevent the satisfaction of (1.3). If

$$\sigma_{sg} - \sigma_{sl} < -\sigma_{lg} \tag{1.4}$$

then θ has passed 180° and (in the absence of gravity) the liquid drop detaches from the surface, an *unwetting* transition. On the other hand, if

$$\sigma_{sg} - \sigma_{sl} > \sigma_{lg} \tag{1.5}$$

then θ passes through 0°, producing a totally flat layer covering the substrate, a *wetting* transition.

Going over to thermodynamic, as opposed to mere mechanical, equilibrium, we imagine the system as *open*, supplied by a particle source to maintain coexistence μ and P. In the complete wetting situation, the boundary substrate then biases the fluid to condense to all liquid,

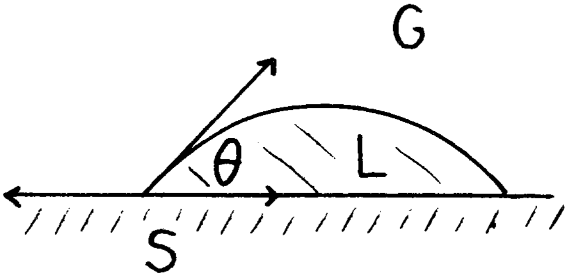

Fig. 1. Mechanical equilibrium for partial wetting.

eliminating any liquid–vapor interface, and when fully nonwet to similarly evaporate to all gas. For partial wetting, in the presence of free evaporation and condensation of droplets, translation invariance along the plane of the substrate—now idealized as an infinite plane—will of course produce a perpendicularly stratified density profile in thermal equilibrium. For the attractive substrate interaction that we have in mind, we anticipate that a dense, liquidlike layer will abut the wall, with gas thereafter (see Fig. 2). However, right at the wall, oscillations of the liquid column should also produce a more gaslike region.

Our objective is to obtain model approximations to the density profile, and, more importantly, to model the qualitative changes occurring under change of controllable parameters. For a simple fluid, we can regard temperature as the controllable parameter. It controls σ_{sg} and σ_{sl} only weakly, since these are principally energetic consequences of the substrate attraction, but the liquid–gas surface tension is a more sensitive function of T, indeed dropping to zero at the critical point. It is clear from (1.4) and (1.5) that as σ_{lg} drops, one passes from nonwetting through partial wetting, and on to the wetting transition. However, the phase-reversed phenomenon of drying (complete liquid → gas layer → all gas) is first analyzed in model form as an indication of the extreme role that fluctuations can play. We follow this with a semiempirical discussion of the normal wetting sequence, emphasizing the distinction between continuous and first-order transitions. A more refined mean field model is then examined to reinforce our conclusions; the two extreme cases of strong, short-range and weak, long-range forces are studied in some detail. The two basic deficiencies of the mean field approximation are finally attended to, that associated with local thermodynamics by a simple set of models, and that associated with neglect of correlations by a Kac–Siegert transformation(8,9) which amalgamates mean field and capillary wave concepts.

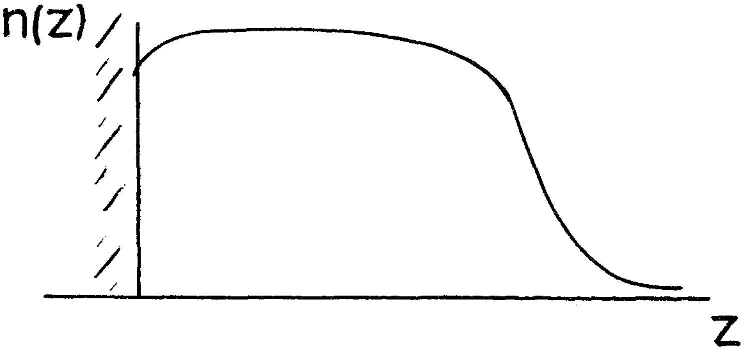

Fig. 2. Density profile for partial wetting.

2. INTERFACE-DOMINATED TRANSITION

The general situation that we will be interested in is that of a structureless, plane-stratified wall characterized by an attractive tail sitting next to a very large repulsion for impenetrability (Fig. 3). The question we first ask is that of drying: whether a liquid column to the right will disappear to infinity, or adhere to the wall. To start, we will adopt a scale in which the intrinsic liquid–gas interface is reduced to a simple discontinuity, being broadened only by thermal motions—capillary waves. On this scale, any microscopic wall layer will not be seen, and our query concerns the existence of a sudden transition between a finite and infinite layer of gas. For analytic tractability, we consider here only a one-dimensional interface of a two-dimensional system.

In this idealized "drumhead model" (Fig. 4) (see, e.g., Ref. 10), the instantaneous interface is specified by the single-valued surface amplitude $\xi(t)$, the gas has density 0, and the incompressible liquid density is ρ, yielding an instantaneous system density

$$\rho(z, t) = \rho\varepsilon(z - \xi(t)) \tag{2.1}$$

The statistical mechanics of this system is easy but not quite trivial. For surface tension σ and shallow surface deformation, the tension energy is

$$\begin{aligned} E_\gamma[\xi] &= \sigma \int \{[1 + \xi(t)^2]^{1/2} - 1\}\, dt \\ &\sim \tfrac{1}{2}\sigma \int \dot{\xi}(t)^2\, dt \end{aligned} \tag{2.2}$$

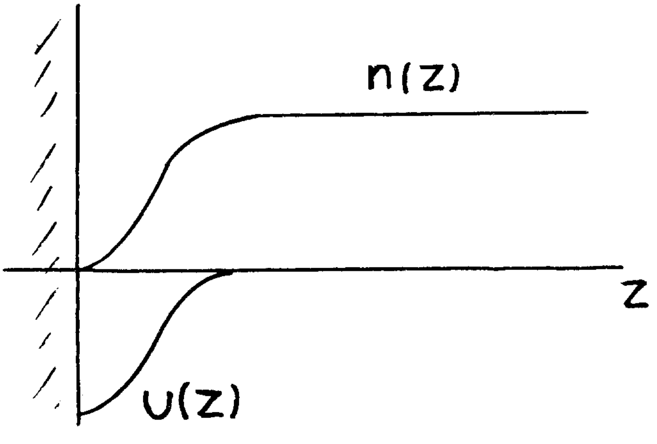

Fig. 3. Configuration for drying transition.

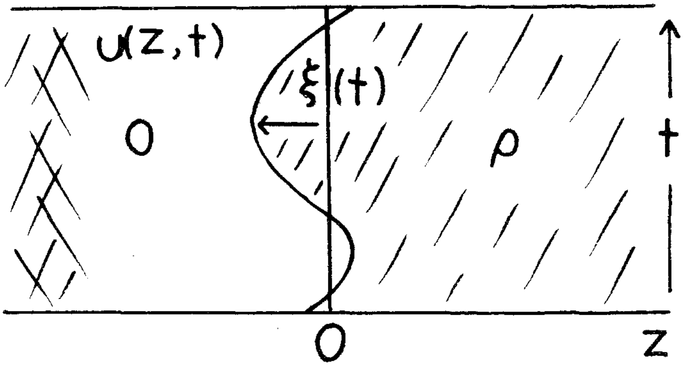

Fig. 4. Drumhead model.

where $\dot{f} = \partial f/\partial t$, while for the field energy

$$\begin{aligned} E_u[\xi] &= \iint \rho(z,t)\, u(z,t)\, dz\, dt \\ &= \rho \iint_{\xi(t)}^{\infty} u(z,t)\, dz\, dt \\ &= \rho \int U(\xi(t),t)\, dt \qquad (2.3) \end{aligned}$$

where $U(\xi, t) = \int_{\xi}^{\infty} u(z,t)\, dz$. The amount of liquid is arbitrary, and so we have $\mu = 0$. Thus the grand canonical partition function becomes

$$\Xi_T = \int \exp -\beta \int \left[\tfrac{1}{2}\sigma\dot{\xi}^2(t) + \rho U(\xi(t),t)\right] dt\, D\xi \qquad (2.4)$$

for appropriate measure $D\xi$. We will leave boundary conditions unspecified.

Since

$$\rho'(z,t) = \rho\delta(z - \xi(t)) \qquad (2.5)$$

where $f' = \partial f/\partial z$, then

$$E_u[\xi] = \iint \rho'(z,t)\, U(z,t)\, dz\, dt \qquad (2.6)$$

and it follows that the profile is determined by

$$n'(z,t) = \langle \rho'(z,t) \rangle = \langle \delta E/\delta U(z,t) \rangle = \delta\Xi_T/\delta U(z,t)$$

or

$$n'(z,t)=\rho\Xi(z,t)\,\hat{\Xi}(z,t)/\Xi_T \tag{2.7}$$

where

$$\Xi(z,t)=\int^{(z,t)} e^{-\beta E[\xi]}\,D\xi$$

$$\hat{\Xi}(z,t)=\int_{(z,t)} e^{-\beta E[\xi]}\,D\xi$$

Since these are standard path integral representations for the diffusion (or Bloch) equation, we have at once[11]

$$\dot{\Xi}=\frac{1}{2\beta\sigma}\Xi''-\beta\rho U\Xi, \qquad -\dot{\hat{\Xi}}=\frac{1}{2\beta\sigma}\hat{\Xi}''-\beta\rho U\hat{\Xi} \tag{2.8}$$

It is not difficult to eliminate Ξ and $\hat{\Xi}$ from (2.7) and (2.8), yielding

$$\frac{1}{2}\frac{\partial}{\partial z}\left(\frac{\dot{n}+n''/2\beta\sigma}{n'}\right)^2-\left(\frac{\partial}{\partial t}-\frac{1}{2\beta\sigma}\frac{\partial^2}{\partial z^2}\right)\frac{\dot{n}+n''/2\beta\sigma}{n'}+\frac{\rho}{\sigma}u=0 \tag{2.9}$$

If $u(z,t)=u(z)$, then with suitable boundary conditions we will have a plane-stratified profile, reducing (2.9) to

$$\frac{1}{2}\frac{1}{(2\beta\sigma)^2}\frac{\partial}{\partial z}\left(\frac{n''}{n'}\right)^2+\frac{1}{(2\beta\sigma)^2}\frac{\partial^2}{\partial z^2}\left(\frac{n''}{n'}\right)+\frac{\rho}{\sigma}u=0 \tag{2.10}$$

or on integrating from z to ∞,

$$-\frac{\partial}{\partial z}\left(\frac{n''}{n'}\right)-\frac{1}{2}\left(\frac{n''}{n'}\right)^2+4\beta^2\sigma\rho U=4\lambda \tag{2.11}$$

for some constant λ. Now setting

$$n'/\rho=\psi^2, \qquad \text{so that} \quad \int\psi^2(z)\,dz=1 \tag{2.12}$$

(using the physically obvious monotonicity of n for our model), we find the basic relation

$$-\tfrac{1}{2}\psi''+\beta^2\sigma\rho U\psi=\lambda\psi \tag{2.13}$$

which is a standard Schrödinger equation.

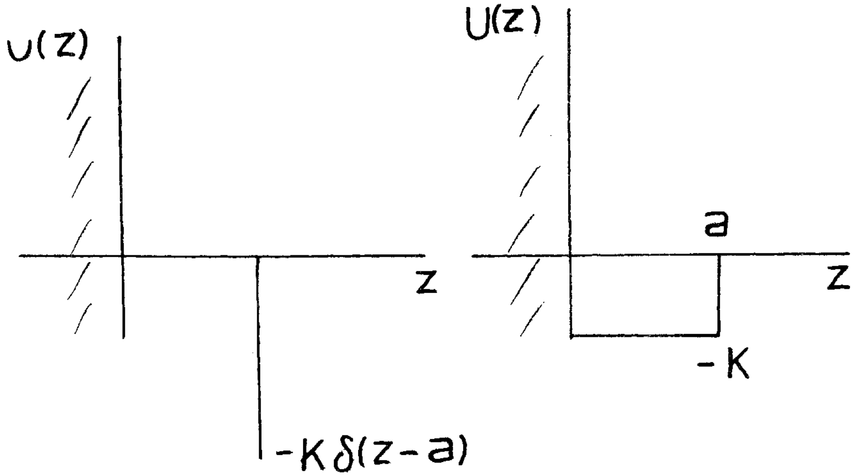

Fig. 5. Prototypical wall potential.

The potential shown in Fig. 5 is prototypical. There are no bound states, i.e., $\psi = 0$ pointwise as soon as σ drops to satisfy

$$Ka^2 \geqslant 1/(2\beta^2\sigma\rho) \tag{2.14}$$

corresponding to liquid pushed out to infinity, whereas there is indeed a bound state, with localized ψ and hence n'—a density rising quickly from 0 to ρ—for σ larger than the limit of (2.14). Thus, there is a wetting transition, albeit of drying type, in this model (see also Refs. 13 and 14). It is interface-dominated in that high σ reduces the surface oscillations, which in turn allows the liquid column to get closer to the substrate attraction.

3. WALL-DOMINATED TRANSITION. PRELIMINARY

When liquid–gas interfacial motions can be neglected, one can speak of the wetting phenomenology as wall-dominated. It is still a matter of balance between substrate-imposed and interfacial energies, but the fluctuational contributions are small in comparison with mean field energies. Let us consider this structure from a highly primitive heuristic viewpoint. Since it is the combination

$$\sigma' = \sigma_{sg} - \sigma_{sl} \tag{3.1}$$

that is expected to play a major role, we will again neglect the gas density—and hence anchor ourselves far from the critical point. Thus, σ' denotes $-\sigma_{sl}$, a positive quantity for a typical attractive wall.

The problem then is that of estimating the substrate attraction and interfacial density gradient contributions to the Helmholtz free energy, and for this purpose we imagine that the interfacial excess energy density profile $\phi_0(z)$, centered at a, is unchanged as a varies (Fig. 6):

$$\phi(z) = \phi_0(z - a)$$

We will suppose that $\phi_0(z)$ has the same form as $-n_0'(z)$ for the particle density profile, but not necessarily the same range. Then we will model the interfacial excess free energy per unit interfacial area (a plane-stratified system is implied)

$$f_l(a) = \int_0^\infty \phi_0(z - a)\, dz \tag{3.2}$$

by the simplest reasonable analytic form

$$f_l(a) = \begin{cases} \sigma(1 - \frac{1}{2}e^{-\lambda a}), & a > 0 \\ \frac{1}{2}\sigma e^{\lambda a}, & a < 0 \end{cases} \tag{3.3}$$

both f_l and its first derivative being continuous at $a = 0$. Here $\sigma = f_l(\infty)$ clearly denotes σ_{lg}.

The substrate interaction contribution to the free energy can be similarly modeled. It, too, should be sigmoidal, reaching its minimum value of $-\sigma'$ when it acts on bulk fluid, and 0 when the fluid is gone, and so we choose

$$f_S(a) = \begin{cases} -\sigma'(1 - \frac{1}{2}e^{-\gamma a}), & a > 0 \\ -\frac{1}{2}\sigma' e^{\gamma a}, & a < 0 \end{cases} \tag{3.4}$$

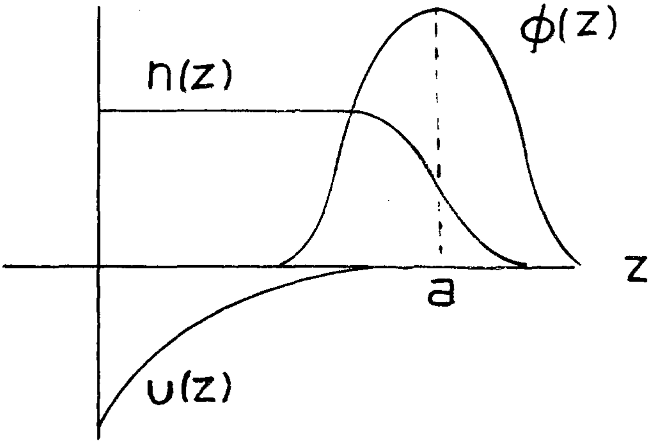

Fig. 6. Potential, density, and free energy density.

γ^{-1} being the effective range of force. Taking $a=0$ as reference, we have for the full free energy $\Delta f(a)=f_l(a)+f_S(a)-f(0)$

$$\Delta f(a)=\begin{cases}\frac{1}{2}\sigma(1-e^{-\lambda a})-\frac{1}{2}\sigma'(1-e^{-\gamma a}), & a>0\\ -\frac{1}{2}\sigma(1-e^{\lambda a})+\frac{1}{2}\sigma'(1-e^{\gamma a}), & a<0\end{cases} \tag{3.5}$$

an odd function, most conveniently. We want to determine the location a that minimizes $\Delta f(a)$. It is of course sufficient to examine the region $a>0$, where $\Delta f(a)$ has at most one stationary value. The basic information we need is that

$$\begin{array}{llll} \text{A.} & \begin{array}{l} f(\infty)>0\\ f(\infty)<0 \end{array} & \text{when} & \begin{array}{l} \sigma'/\sigma<1\\ \sigma'/\sigma>1 \end{array}\\[2ex] \text{B.} & \begin{array}{l} f'(0)>0\\ f'(0)<0 \end{array} & \text{when} & \begin{array}{l} \sigma'/\sigma<\lambda/\gamma\\ \sigma'/\sigma>\lambda/\gamma \end{array}\\[2ex] \text{C.} & \begin{array}{l} f'(a\to\infty)>0\\ f'(a\to\infty)<0 \end{array} & \text{when} & \begin{array}{l} \lambda/\gamma<1\\ \lambda/\gamma>1 \end{array} \end{array} \tag{3.6}$$

Using (3.6), we can now see how the free energy minimum changes as temperature increases with consequent decrease of σ. First, for short-range wall attraction in the sense that $\lambda/\gamma<1$, we have the results shown in Fig. 7, where the minimum is indicated with a cross (×). We see that there

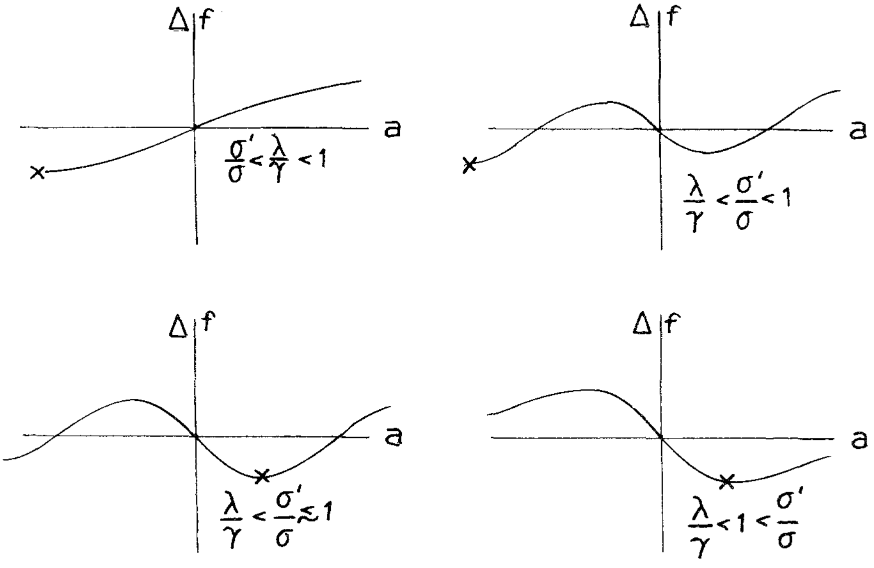

Fig. 7. Plot of Δf versus a for short-range potential, $\lambda/\gamma<1$.

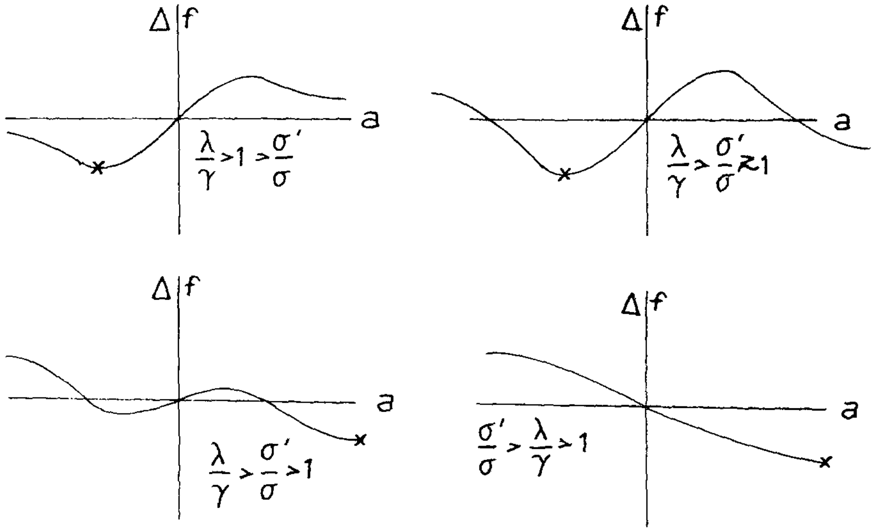

Fig. 8. Plot of Δf versus a for long-range potential, $\lambda/\gamma > 1$.

is a first-order dewetting transition, which takes place when the internal minimum reaches the $a = -\infty$ minimum. This is readily computed to be at

$$1-\frac{\sigma'}{\sigma}=\frac{1}{2}\left(\frac{\sigma\lambda}{\sigma'\lambda}\right)^{\lambda/(\gamma-\lambda)}\left(1-\frac{\lambda}{\gamma}\right) \tag{3.7}$$

Interestingly, this model does not seem to go on to the wetting transition. However, since the effective range γ^{-1} will certainly increase as well, as σ drops, a continuous transition can readily be imagined.

For long-range wall attraction, $\lambda/\gamma > 1$, we similarly find the result in Fig. 8, which always shows a jump from finite to infinite a, a first-order wetting transition.

4. MEAN FIELD MODEL

Let us now elaborate the hand-waving discussion of the preceding section in the microscopic domain. The key approximation is that density fluctuations can be neglected, and the intelligent way of using this is in the context of the van der Waals mean field model (originating in Ref. 15). For this purpose, the pair interaction potential is divided into a short-range repulsive core and a long-range attractive tail (Fig. 9):

$$\phi(r)=\phi_0(r)-\phi_1(r) \tag{4.1}$$

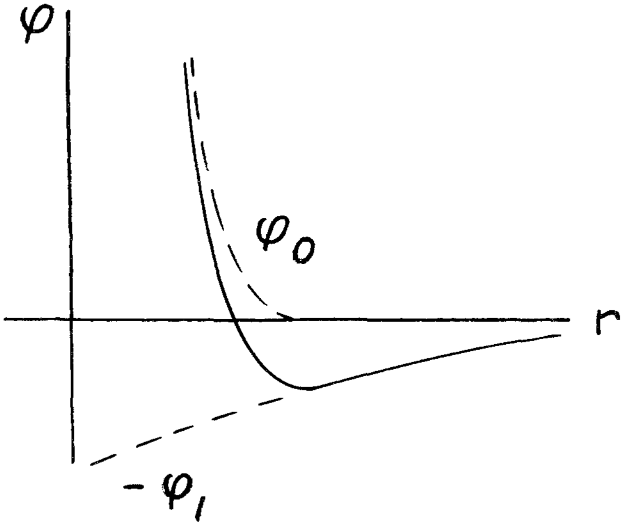

Fig. 9. Van der Waals decomposition of pair interaction.

Fluctuations at the core level are not neglected, but rather encompassed by regarding the core fluid as in local bulk equilibrium, represented by a Helmholtz free energy

$$F_0[n] = \int f_0(n(r))\, n(r)\, d^3r \tag{4.2}$$

where $f_0(n)$ is the per-particle free energy. Fluctuations at the tail level are, however, specifically neglected by choosing the tail energy contribution as

$$F_1[n] = -\frac{1}{2}\iint \phi_1(r-r')\, n(r)\, n(r')\, d^3r\, d^3r' \tag{4.3}$$

In the presence of an external potential $u(r)$, the bulk or internal Helmholtz free energy is thus modeled as

$$\begin{aligned} F^B &= F - \int n(r)\, u(r)\, d^3r \\ &= \int f_0(n(r))\, n(r)\, d^3r - \frac{1}{2}\iint \phi_1(r-r')\, n(r)\, n(r')\, d^3r\, d^3r' \end{aligned} \tag{4.4}$$

In particular, for a uniform fluid, we have

$$\begin{aligned} F/V &= nf_0(n) - \tfrac{1}{2}\phi_1 n^2 \\ \mu &= \partial(F/V)/\partial n = \mu_0(n) - \phi_1 n \\ P &= -\partial F/\partial V = P_0(n) - \tfrac{1}{2}\phi_1 n \end{aligned} \tag{4.5}$$

where $\phi_1 = \int \phi_1(r)\, d^3r$. The mean field profile equation now follows as usual from (4.4) by functional differentiation

$$\begin{aligned} \mu - u(r) &= \delta F^B/\delta n(r) \\ &= \mu_0(n(r')) - \int \phi_1(r - r')\, n(r')\, d^3r' \end{aligned} \tag{4.6}$$

Specializing to plane stratification, this reduces to

$$\mu - u(z) = \mu_0(n(z)) - 2\pi \int \phi_2(z - z')\, n(z')\, dz' \tag{4.7}$$

where $\phi_2(z) = \int_z^\infty r\phi_1(r)\, dr$.

Explicit solution of (4.7) is available in only a few cases. One is that of van der Waals, in which $\phi_1(r)$ is represented by a combination of $\delta(r)$ and $\nabla^2\delta(r)$. A more reasonable choice from the point of view of internal consistency(16,17) is that of a Yukawa function

$$\phi_1(r) = Ae^{-r}/r \tag{4.8}$$

(with $\phi_1 = 4\pi A$), the range here being normalized to unity. Thus

$$\phi_2(z) = Ae^{-|z|} \tag{4.8$'$}$$

and choosing for convenience μ_0 rather than $n(z)$ as dependent variable, we then obtain for (4.7)

$$\mu - u(z) = \mu_0(z) - 2\pi A \int e^{-|z - z'|} n_0(\mu_0(z'))\, dz' \tag{4.9}$$

where n_0 is the thermodynamic function inverse to μ_0.

Equation (4.9) can now be processed by successive differentiation:

$$-u'(z) = \mu_0'(z) + 2\pi A \int \operatorname{sgn}(z - z')\, e^{-|z - z'|} n_0(\mu_0(z'))\, dz' \tag{4.10a}$$

$$-u''(z) = \mu_0''(z) + 4\pi A n_0(\mu_0(z)) - 2\pi A \int e^{-|z - z'|} n_0(\mu_0(z'))\, dz' \tag{4.10b}$$

(4.9) and (4.10b) yield at once the "equation of motion"

$$\mu_0''(z) - \mu_0(z) + 4\pi A n_0(\mu_0(z)) + u''(z) - u(z) + \mu = 0 \tag{4.11}$$

We also need boundary conditions. For a hard wall to the left of $z = z_0$, we have $n(z) = 0$ for $z \leqslant z_0$, so that from (4.9) and (4.10a)

$$\begin{aligned} \mu - u(z_0) &= \mu_0(z_0) - 2\pi A \int_{z_0}^\infty e^{-(z - z_0)} n_0(\mu_0(z'))\, dz' \\ -u'(z_0) &= \mu_0'(z_0) - 2\pi A \int_{z_0}^\infty e^{-(z - z_0)} n_0(\mu_0(z'))\, dz' \end{aligned} \tag{4.12}$$

yielding the boundary condition[(18)]

$$\mu_0'(z_0) - \mu_0(z_0) + u'(z_0) - u(z_0) + \mu = 0 \tag{4.13}$$

In the absence of an external potential, using the thermodynamic $n_0\, d\mu_0 = dP_0$, we can integrate (4.11) at once to

$$\frac{1}{2\pi A}\mu_0'(z)^2 - \frac{1}{8\pi A}[\mu_0(z) - n]^2 + P_0(\mu_0(z)) = P \tag{4.14}$$

If (4.14) is to correspond to a gas–liquid interface leading to bulk densities $n_0(\infty) = n_G$, $n_0(-\infty) = n_L$, then according to (4.5), we need

$$\begin{gathered}\mu_L - 4\pi A n_L = \mu = \mu_G - 4\pi A n_G \\ P_0(\mu_L) - 2\pi A n_L^2 = P = P_0(\mu_G) - 2\pi A n_G^2\end{gathered} \tag{4.15}$$

where $\mu_G = \mu_0(n_G)$, $\mu_L = \mu_0(n_L)$. This shows that P in (4.14) is the system pressure, and that the "potential function" (Fig. 10)

$$V(\mu_0) = P_0(\mu_0) - \frac{1}{8\pi A}(\mu_0 - \mu)^2 \tag{4.16}$$

has equal maxima at μ_G and μ_L.[(16,17)]

Note that if a wall is now inserted at $z = 0$, then (4.13) in the form

$$\mu_0(0) - \mu = \mu_0'(0) \qquad \text{at a wall} \tag{4.17}$$

locates the profile (4.14) by the condition $P_0(\mu_0(0)) = P$, or

$$V(\mu_0(0)) = P - \frac{1}{2\pi A}[\mu_0(0) - \mu]^2 \tag{4.18}$$

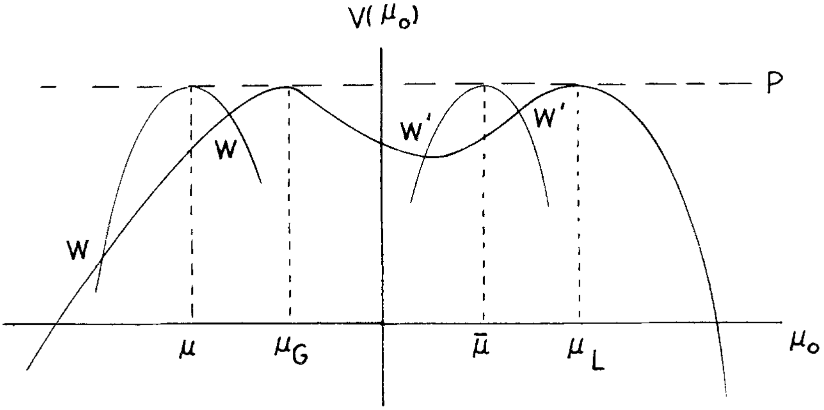

Fig. 10. Potential function for μ_0 profile.

The corresponding intersections W are of course pure gas phase, but in fact only one is possible: since μ_0 decreases from μ_G at ∞ to its wall value, and since μ_0' cannot change sign in the interval, one has $\mu_0(0) - \mu = \mu_0'(0) > 0$, so that only the right intersection is valid.

5. LIMITING CASES

Proceeding now to wetting, we imagine first a very strong, short-range attraction, i.e., assume

$$\begin{aligned} -1 &\gg \beta u(z) \qquad \text{for} \quad -b \leqslant z \leqslant 0 \\ u(z) &= 0 \qquad\quad \text{for} \quad z > 0 \end{aligned} \tag{5.1}$$

with the wall at $z_0 = -b$. It is convenient to switch to

$$v(z) = \mu_0(z) + u(z) \tag{5.2}$$

as dependent variable, so that

$$\begin{aligned} v''(z) - v(z) + 4\pi A n_0[v(z) - u(z)] + \mu &= 0 \\ v'(-b) - v(-b) + \mu &= 0 \end{aligned} \tag{5.3}$$

Clearly, v and v' are continuous at $z = 0$, and $n_0(v(z) - u(z)) = n_c$, the close-packing density, for $-b < z \leqslant 0$. Given $v(0) = \mu_0(0)$ and $v'(0) = \mu_0'(0) < 0$, (5.3) is then trivial to solve in the region $-b \leqslant z \leqslant 0$, yielding the displaced boundary condition

$$\mu_0'(0) - \mu_0(0) + \mu + 4\pi A n_c(1 - e^{-b}) = 0 \tag{5.4}$$

for the field-free fluid to the right of $z = 0$.

Equation (5.4) now replaces (4.17), locating the $z \geqslant 0$ profile in μ_0 space by the condition

$$V(\mu_0(0)) = P - \frac{1}{8\pi A}[\mu_0(0) - \bar{\mu}]^2 \tag{5.5}$$

where $\bar{\mu} = \mu + 4\pi A n_c(1 - e^{-b})$ emanating from (4.14) and (4.16). Thus, $z = 0$ corresponds to the intersection points W' shown, of which only the left is consistent—see argument following (4.18)—with physics. At fixed b, $\bar{\mu}$ increases with increasing temperature, driving the intersection points toward μ_L, at which point a continuous transition to pure liquid takes place. The condition for the wetting transition is thus $\mu_L = \mu + 4\pi A n_c(1 - e^{-b})$, or, by (4.15),

$$n_L = n_c(1 - e^{-b}) \tag{5.6}$$

An intermediate-range case has been solved by Sullivan. It is that in which the wall is at $z_0 = 0$ and

$$u(z) = -\varepsilon e^{-z} \tag{5.7}$$

the same range as the internal interactions. Since $\mu''(z) - u(z) = 0$, (4.11) again implies (4.14), and (4.13) now reduces to

$$\mu_0'(0) - \mu_0(0) + \mu + 2\varepsilon = 0 \tag{5.8}$$

Hence the wall is determined by (5.5), with

$$\bar{\mu} = \mu + 2\varepsilon \tag{5.9}$$

The analysis is therefore precisely as in the strong potential case, with a necessarily continuous wetting transition with rise of temperature, occurring when

$$n_L = \varepsilon/2\pi A \tag{5.10}$$

Let us now go to the extremely weak, long-range wall potential. We will paraphrase an elegant analysis of Aukrust and Hauge$^{(19)}$ (see also Refs. 20–22). To do so, we first observe that the equation of motion (4.11) is the result of minimizing the quantity

$$\sigma_T[\mu_0] = \int_{z_0}^{\infty} \left\{ -P_0(\mu_0(z)) + P \right. \\ \left. + \frac{1}{8\pi A} [\mu_0'(z) + u'(z) + \mu - \mu_0(z) - u(z)]^2 \right\} dz \tag{5.11}$$

and that the boundary condition (4.13) is likewise the result of the free variation of $\mu_0(z_0)$ in (5.11)—the so-called "natural" boundary condition. The physical meaning of (5.11) is found by first using (4.9) with (4.10a):

$$\mu_0'(z) + u'(z) + \mu - \mu_0(z) - u(z) = -4\pi A \int_{z_0}^{z} e^{-|z-z'|} n(z')\, dz' \tag{5.12}$$

to transform the second part of (5.11), and then (4.9) itself to reexpress the first part, resulting in

$$\sigma_T[\mu_0] = \int_{z_0}^{\infty} [f_0(n(z))\, n(z) + u(z)\, n(z) + P - n(z)\mu]\, dz \\ - \pi A \iint_{z_0}^{\infty} e^{-|z-z'|} n(z)\, n(z')\, dz\, dz' \tag{5.13}$$

which is precisely the excess free energy due to the two interfaces.

Returning to the wetting problem, if the interaction with the wall is indeed weak, we can solve perturbatively (see Ref. 23 for a neat direct approach) by using the field-free profile as variational ansatz. There are two problems. First, the field-free profile is undetermined by a common translation, so that we shall take

$$\mu_0(z)=\mu_S(z-a) \tag{5.14}$$

where the standard profile $\mu_S(z)$ is defined, e.g., by $|\mu_S'(z)|=\text{Max}$ at $z=0$. Second, one expects a boundary layer near the wall, and corresponding energy contributions. However, if this "heals" well before the liquid–gas interface—which will be far away for a long-range potential—its form will not change, and it can be neglected. Thus, instead of (5.11) we can use the variational expression (set the wall at $z=0$)

$$\begin{aligned}\sigma_T(a)=\int_0^\infty \Big\{&-P_0(\mu_0(z-a))+P\\ &+\frac{1}{8\pi A}\left[\mu_S'(z-a)-\mu_S(z-a)+\mu+u'(z)-u(z)\right]^2\Big\}\,dz\end{aligned} \tag{5.15}$$

To assess a wetting transition, we will be interested in comparing this to the fully wet situation:

$$\Delta\sigma_T(a)=\sigma_T(a)-\sigma_T(\infty)=Q(a)+R(u,a)$$

where

$$\begin{aligned}Q(a)=\int_0^\infty \Big\{&P_0(\mu_L)-P_0(\mu_S(z-a))\\ &+\frac{1}{8\pi A}\left[\mu_S'(z-a)-\mu_S(z-a)+\mu_L\right]\\ &\times\left[\mu_S'(z-a)-\mu_S(z-a)+2\mu-\mu_L\right]\Big\}\,dz\end{aligned} \tag{5.16}$$

$$R(u,a)=-\int_0^\infty \frac{1}{4\pi A}\left[\mu_S'(z-a)-\mu_S(z-a)+\mu_L\right]\left[u(z)-u'(z)\right]dz$$

If the scale of variation of $u(z)$ is much longer than that of $u_S(z)$, analysis of (5.16) is highly insensitive to details of either. This behavior is mainly due to the second, potential-dependent term $R(u,a)$. It is only necessary to use the identity

$$\int_0^\infty f(z)\, g(z)\, dz$$

$$= f(0) \int_0^a g(z)\, dz + f(\infty) \int_a^\infty g(z)\, dz \tag{5.17}$$

$$+ \int_0^a [f(z) - f(0)]\, g(z)\, dz + \int_0^\infty [f(z) - f(\infty)]\, g(z)\, dz$$

where the second line can be dropped if the variation of f is restricted to the region around a. Hence

$$R(u, a) \simeq -\frac{\mu_L - \mu_G}{4\pi A} \int_a^\infty [u(z) - u'(z)]\, dz \tag{5.18}$$

with the form shown in Fig. 11. Now $Q(a)$ reaches its asymptotic value of 0 at a much smaller value of a. It is therefore clear that if $Q(a)$ dips low enough to render $\Delta\sigma_T(a) < 0$—partial wetting at finite a—a weakening of this dip produces a minimum $\Delta\sigma_T(a)$ at $a = \infty$, necessarily a discontinuous first-order transition.

Assessment is normally made, not in terms of the model parameter a, but rather in terms of the coverage

$$\Gamma = \int_0^\infty [n(z) - n_G]\, dz \tag{5.19}$$

translating via (4.11) to

$$4\pi A\Gamma = \int_0^\infty [\mu_0(z) + u(z) - \mu_G]\, dz + \mu'(0) + u(0) \tag{5.20}$$

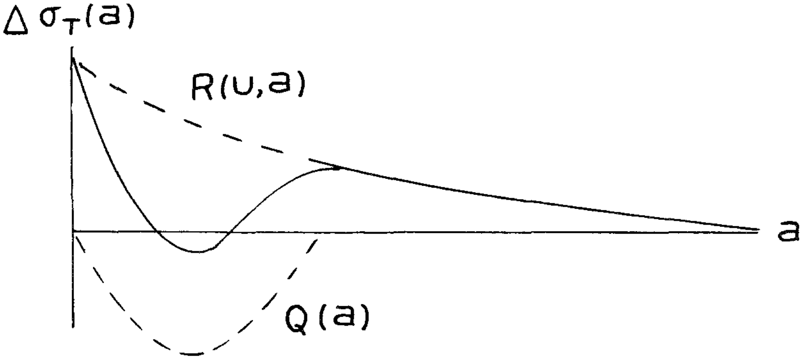

Fig. 11. Component free energies for long-range potential.

Divergence of (5.19) is associated, via sum rules (see, e.g., Refs. 24 and 25) with large interfacial fluctuations, but we will use this information merely to motivate our return to the question of techniques for improving the basic mean field model.

6. LOCAL CORRECTIONS

For the system at hand, the van der Waals approach is inadequate in both of its assumptions (but see Ref. 26). The adsorbed layer at the wall can change its density very rapidly, so that local core thermodynamics will not do, and large-scale density waves—the capillary waves we have already examined—make the use of mean field itself suspect. Let us see how one might correct for these effects.(27–30)

Suppose then that the core fluid density cannot be regarded as locally constant. The most direct correction procedure is that in which one chooses a uniform reference density $\bar{n}$ with no external field, and expands the quantity $\mu - u(r) - \mu_0(r')$, which would vanish for slowly varying density. Since

$$\frac{\delta\mu - u(r)}{\delta n(r')} = \frac{1}{\beta}\left[\frac{\delta(r-r')}{n(r)} - c_{20}(r, r')\right] \tag{6.1}$$

where c_{20} is the core direct correlation function, and since $\mu - u(r) = \mu_0(\bar{n})$ initially, we have to first order

$$\begin{aligned}&\mu - u(r) - \mu_0(n(r))\\ &\quad = \int \left\{\frac{1}{\beta}\left[\frac{\delta(r-r')}{\bar{n}} - c_{20}(r-r')\right] - \mu_0'(\bar{n})\,\delta(r-r')\right\}[n(r') - \bar{n}]\,d^3r'\end{aligned} \tag{6.2}$$

where c_{20} is evaluated at $\bar{n}$. But

$$\int c_{20}(r-r')\,d^3r' = [1 - \beta P_0'(\bar{n})]/\bar{n} = [1 - \bar{n}\mu_0'(\bar{n})]/\bar{n}$$

and so

$$\begin{aligned}\mu - u(r) = \mu_0(n(r)) &+ \left[\frac{1}{\beta\bar{n}} - \mu_0'(\bar{n})\right] n(r)\\ &- \frac{1}{\beta}\int c_{20}(r-r')\,n(r')\,d^3r'\end{aligned} \tag{6.3}$$

Hence, to this order, (4.6) still applies, but with a modified $\mu_0(n)$ and a modified $\phi_1(r-r')$.

Higher accuracy expansions are available, e.g., expanding about $n(r)$ rather than $\bar{n}$, but in conformity with the tenor of our discussion, we will instead treat the matter of core fluid inhomogeneity from a model viewpoint. The primitive model is that of a nonuniform, one-dimensional, diameter-a, hard-rod fluid.(31) This is most readily solved(32) by observing that the grand partition function

$$\Xi(x) = \sum_{N=0}^{\infty} \int_{x_1 + a \leqslant x_2, \ldots, x_N + a \leqslant x} \exp\left[\beta \sum_1^N u(x_i)\right] dx_1 \cdots dx_N \tag{6.4}$$

in the box $(-\infty, x)$ satisfies

$$\frac{\partial}{\partial x} \Xi(x+a) = e^{\beta(\mu - u(x))} \Xi(x) \tag{6.5}$$

Thus, setting

$$\Xi(x) = \exp \beta \int_{-\infty}^{x} P(y)\, dy \tag{6.6}$$

we have

$$\mu - u(x) = \beta \int_{x}^{x+a} P(y)\, dy + \frac{1}{\beta} \ln \beta\, P(x+a) \tag{6.7}$$

As a consequence,

$$\frac{\delta[\mu - u(x)]}{\delta P(y)} = \varepsilon(x + a - y) - \varepsilon(x - y) + \frac{\delta(x + \varepsilon - y)}{\beta P(y)} \tag{6.8}$$

But since the grand potential is given by $\Omega = -(1/\beta) \ln \Xi(\infty)$, the sequence

$$\begin{aligned} 1 &= \int \delta(z-y)\, dz \\ &= \iint \frac{\delta P(z)}{\delta[\mu - u(x)]} \frac{\delta[\mu - u(x)]}{\delta P(y)}\, dx\, dz \\ &= \int \frac{\delta \Omega}{\delta[\mu - u(x)]} \frac{\delta[\mu - u(x)]}{\delta P(y)}\, dx \\ &= \int_{y-a}^{y} n(x)\, dx + \frac{n(y-a)}{\beta P(y)} \end{aligned}$$

then establishes

$$\beta P(y) = \frac{n(y-a)}{1 - \int_{y-a}^{y} n(z)\, dz} \tag{6.9}$$

For the thermodynamics, we now have

$$\Omega = -\int n(y-a) \Big/ \left[1 - \int_{y-a}^{y} n(y)\, dy \right] dz$$

which is readily transformed to

$$\Omega = -\frac{1}{2} \int \left[n\left(y+\frac{a}{2}\right) + n\left(y-\frac{a}{2}\right) \right] \Big/ \left[1 - \int_{y-a/2}^{y+a/2} n(y)\, dy \right] dz$$

which we write as

$$\Omega = -\int \frac{n_\sigma(y)}{1 - a n_\tau(y)}\, dy \tag{6.10}$$

The weighted densities here are defined by

$$n_w(x) = \int w(z)\, n(x+z)\, dz, \qquad \int w(z)\, dz = 1 \tag{6.11}$$

where

$$\tau'(y) = \frac{1}{a}\, \varepsilon\left(\frac{a}{2} - |y|\right)$$

produces a volume average, and

$$\sigma(y) = -y\tau'(y) = \frac{1}{2}\left[\delta\left(y - \frac{a}{2}\right) + \delta\left(y + \frac{a}{2}\right) \right]$$

produces a surface average via an infinitesimal dilation. Generalization to non-hard core–core interactions in three dimensions is now obvious. One writes instead

$$\Omega_0 = \int n_0(r)\, \omega_0(n_\tau(r))\, d^3r \tag{6.12}$$

where $\omega_0(n) = -P_0(n)/n$, the weights τ and σ thus being available to satisfy any further conditions we may wish to impose.

With (6.12), we can now return to the profile, which is best obtained indirectly. We first separate the ideal gas and "excess" parts:

$$\begin{aligned} \Omega_0 &= -\frac{1}{\beta} \int n(r)\, d^3r + \int n_0(r)\, \omega_0^{\mathrm{ex}}(n_\tau(r))\, d^3r \\ \omega_0^{\mathrm{ex}}(n) &= \omega_0(n) + \frac{1}{\beta} \end{aligned} \tag{6.13}$$

and then use the relation

$$\left[1-\int n(r)\frac{\delta}{\delta n(r)}\,d^3r\right]F_0^\beta=\Omega_0 \tag{6.14}$$

to obtain

$$F_0^B=\frac{1}{\beta}\int n(r)[\ln n(r)-1]\,d^3r+\int n_\sigma(r)\,f_0^{\text{ex}}(n_\tau(r))\,d^3r \tag{6.15}$$

where

$$f_0^{\text{ex}}(n)=f_0(n)+\frac{1}{\beta}-\frac{1}{\beta}\ln n$$

Differentiating with respect to $n(r)$, we find

$$\begin{aligned}\mu-u(r)={}&\frac{1}{\beta}\ln n(r)+\int\sigma(r-r')\,f_0^{\text{ex}}(n_\tau(r'))\,d^3r'\\&-\int n_\sigma(r')\,\tau(r-r')\,\omega_0^{\text{ex}}(n_\tau(r'))/n_\tau(r')\,d^3r'\end{aligned} \tag{6.16}$$

Equation (6.16), irrespective of the choice of τ and σ, is readily shown to satisfy the important action–reaction sum rule

$$\int n(z)\,u'(z)\,dz+P_0=0 \tag{6.17}$$

when bounded by a stratified potential on the left but free on the right.

One obvious criterion for choosing τ and σ is to demand that they yield the correct direct correlation at some uniform reference density $\bar{n}$. From (6.1), this is seen to require

$$c_{20}(r)=-2B_{20}(\bar{n})\,\sigma*\tau(r)-\bar{n}B_{20}'(\bar{n})\,\tau*\tau(r) \tag{6.18}$$

where $B_2(n)=[\beta P(n)-n]/n^2$, or in Fourier transform

$$\tilde{c}_{20}(k)=-2B_{20}(\bar{n})\,\tilde{\sigma}(k)\,\tilde{\tau}(k)-\bar{n}B_{20}'(\bar{n})\,\tilde{\tau}'(k)^2 \tag{6.19}$$

at the reference density $\bar{n}$. For the remaining relation between σ and τ, several options are available. One is to demand that (6.19) hold at two reference densities. Another is to again produce σ by an infinitesimal dilation

$$\sigma(r)=-\tfrac{1}{3}r\cdot\nabla\tau(r) \tag{6.20}$$

to be used in conjunction with (6.19), or even with an empirical volume average. Perhaps simplest is the choice $\sigma(r) = \tau(r)$ (with hard rods no longer a special case), so that (6.16) and (6.19) reduce to

$$\mu - u(r) = \frac{1}{\beta} \ln n(r) + \overline{\mu_0^{\text{ex}}(\bar{n}(r))} \tag{6.21}$$

where

$$\begin{aligned} \bar{f}(r) &= \int \tau(r')\, f(r+r')\, d^3r' \\ \tilde{\tau}(k)^2 &= \tilde{c}_{20}(k)/\tilde{c}_{20}(0) \end{aligned} \tag{6.21}$$

Few of these possibilities have been investigated in detail.

7. MEAN FIELD CORRECTIONS

Let us now shift our attention to long-wavelength behavior. For this purpose, we can deal with the core fluid on a local thermodynamic basis, and focus on correlation corrections to the mean field picture. The van der Waals decomposition (4.1) is still the format of choice, but we want to associate thermalized particles with the short-range forces, and waves with that portion of longer range. An appropriate starting form is

$$\begin{aligned} \Xi[\mu - u] = \operatorname{Tr}\bigg(&\exp \beta \left\{ \int \rho(r)[\mu - u(r)]\, d^3r - \Phi_0[\rho] \right\} \\ &\times \exp\left[\frac{1}{2}\beta \iint \rho(r)\, \phi_1(r-r')\, \rho(r')\, d^3r\, d^3r'\right]\bigg) \end{aligned} \tag{7.1}$$

where $\rho(r) = \sum \delta(r - r_j)$ is the microscopic density, $\Phi[\rho]$ is the corresponding (bilinear) core energy, μ includes the ϕ_1 self-interaction, and Tr integrates over all particles involved. The desired dual representation (Kac–Seigert$^{(8,9)}$) makes use of the Gaussian functional integral

$$\begin{aligned} &\exp\left[\frac{1}{2}\beta \iint \rho(r)\, \phi_1(r-r')\, \rho(r')\, d^3r\, d^3r'\right] \\ &\quad = \int \exp\left[-\frac{1}{2}\beta \iint v(r)\, \phi_1^{-1}(r-r')\, v(r')\, d^3r\, d^3r'\right] \\ &\quad\quad \times \exp\left[-\beta \int v(r)\, \rho(r)\, d^3r\right] Dv \end{aligned} \tag{7.2}$$

where Dv is an appropriate measure, and $\phi_1^{-1}(r-r')$ is the inverse of ϕ_1 regarded as the kernel of an integral operator. It follows at once that

$$\Xi[\mu-u]=\int \exp\left[-\frac{1}{2}\beta\iint v(r)\,\phi_1^{-1}(r-r')\,v(r')\,d^3r\,d^3r'\right] \times \Xi_0[\mu-u-v]\,Dv \tag{7.3}$$

which we write (see, e.g., Ref. 32) in the compact form of a v-space partition function

$$e^{-\beta\Omega[\mu-u]}=\int e^{-\beta H_u[v]}\,Dv$$

$$H_u[v]=\Omega_0[\mu-u-v]+\frac{1}{2}\iint v(r)\,\phi_1^{-1}(r-r')\,v(r')\,d^3r\,d^3r' \tag{7.4}$$

and associated v-space probability distribution

$$p_u[v]=e^{\beta(\Omega[\mu-u]-H_u[v])} \tag{7.5}$$

Our major interest is in the profile

$$n(r)=\delta\Omega[\mu-u]/\delta u(r) \tag{7.6}$$

In the local thermodynamics approximation,

$$\Omega_0[\mu-u-v]=\int \omega_0(\mu-u(r)-v(r))\,n_0(\mu-u(r)-v(r))\,d^3r \tag{7.7}$$

where ω_0 and n_0 are functions, not functionals of their respective arguments, so that (7.6) attains the simple form

$$n(r)=\langle n_0(\mu-u(r)-v(r))\rangle_{p_u[v]} \tag{7.8}$$

i.e., the internal field ϕ_1 has been simulated by an ensemble of external fields $\{v\}$. To evaluate (7.8), we can proceed by steepest descent. In zeroth order, we simply use that function $\bar{v}(r)$ that maximizes $p_u[v]$:

$$0=\frac{\delta H_u[\bar{v}]}{\delta\bar{v}(r)}=n_0(\mu-u(r)-\bar{v}(r))+\int \phi_1^{-1}(r-r')\,\bar{v}(r')\,d^3r' \tag{7.9}$$

Hence

$$\begin{aligned}\bar{v}(r)&=-\int \phi_1(r-r')\,n_0(\mu-u(r')-\bar{v}(r'))\,d^3r'\\ &=-\int \phi_1(r-r')\,n(r')\,d^3r'\end{aligned} \tag{7.10}$$

is precisely the mean field that gives rise to (4.6).

We now continue by expanding in $\Delta(r) = v(r) - \bar{v}(r)$. Since

$$\frac{\delta^2 H_u[\bar{v}]}{\delta\bar{v}(r)\,\delta\bar{v}(r')} = -n_0'(\mu - u(r) - \bar{v}(r))\,\delta(r-r') + \phi_1^{-1}(r-r')$$

$$= -\frac{\delta(r-r')}{\mu_0'(\bar{n}(r))} + \phi_1^{-1}(r-r') \tag{7.11}$$

where $\bar{n}(r)$ is the mean field profile, (7.8) then becomes, through second order,

$$n(r) = \int n_0(\mu - u(r) - \bar{v}(r) - \Delta(r))$$

$$\times \int \frac{\exp[-\frac{1}{2}\beta \iint M(r,r')\,\Delta(r)\,\Delta(r')\,d^3r\,d^3r']}{\exp[-\frac{1}{2}\beta \iint M(r,r')\,\Delta(r)\,\Delta(r')\,d^3r\,d^3r']\,D\Delta}$$

where

$$M(r,r') = -\delta(r-r')/\mu_0'(\bar{n}(r)) + \phi_1^{-1}(r-r') \tag{7.12}$$

Only $\Delta(r)$ at fixed r occurs in the integrand, allowing us to reduce (7.12) at once to

$$n(r) = \int n_0(\mu - u(r) - \bar{v}(r) - \Delta)\exp\left[-\frac{1}{2}\Delta^2/M^{-1}(r,r)\right]d\Delta$$

$$\times [2\pi M^{-1}(r,r)]^{-1/2} \tag{7.13}$$

which is just an r-dependent Gaussian spread of μ, due to the excitations represented by the normal modes of M. For a clearer interpretation, if Δ is not large on the scale of $\bar{v}$, we can write $\bar{v}(r) + \Delta = \bar{v}(r + \hat{\eta}\Delta/|\nabla\bar{v}'(r)|)$, where $\hat{\eta}$ is the unit vector in the direction $\nabla\bar{v}(r)$. Hence, (7.13) becomes

$$n(r) = \int n_0(\mu - u(r) - \bar{v}(r + \xi A(r)\,\hat{\eta}))\,e^{-1/2\xi^2}\,d\xi/(2\pi)^{1/2} \tag{7.14}$$

where

$A^2(r) = M^{-1}(r,r)/|\nabla\bar{v}(r)|$. We recognize the profile broadening as due to the mean field being carried bodily by the correlated motion $r \to r + \xi A(r)\,\hat{\eta}$ with Gaussian distribution of ξ, an obvious manifestation of capillary waves.

It is to be observed that (7.14)—determined by $\bar{n}(r)$—will transcribe any fluctuationless profile to its fluctuation-broadened image, but will not, e.g., change the nature of the underlying wetting transition. One can readily imagine self-consistent generalizations in which this is not the case. For further discussion, see Ref. 33.

ACKNOWLEDGMENT

This work was supported in part by NSF grant CHE-8b-07598 and DOE contract DE-AC02-76ER03077.

REFERENCES

1. W. F. Saam and C. Ebner, *Phys. Rev. A* **17**:1768 (1978).
2. R. Pandit, M. Schick, and M. Wortis, *Phys. Rev. B* **26**:5112 (1982).
3. E. H. Hauge and M. Schick, *Phys. Rev. B* **27**:4288 (1983).
4. E. H. Hauge, in *Fundamental Problems in Statistical Mechanics, VI*, E. G. D. Cohen, ed. (Elsevier, 1985).
5. E. H. Hauge, *Phys. Rev. B* **33**:3322 (1986).
6. A. K. Sen and C. Ebner, *Phys. Rev. B* **33**:5076 (1986).
7. C. Ebner and W. F. Saam, *Phys. Rev. B* **35**:1822 (1987).
8. M. Kac, in *Applied Probability* C. A. MacColl, ed. (McGraw-Hill, 1957).
9. A. J. F. Siegert, *Physica (Suppl.)* **26**:S30 (1960).
10. D. Jasnow and J. Rudnick, *Phys. Rev. Lett.* **41**:698 (1978).
11. R. P. Feynman and A. R. Hibbs, *Quantum Mechanics and Path Integrals* (McGraw-Hill, 1965), Chapter X.
12. J. K. Percus, *J. Chem. Phys.* **81**:452 (1984).
13. R. Lipowsky, D. M. Kroll, and R. K. P. Zia, *Phys. Rev. B* **27**:4499 (1983).
14. D. M. Kroll and R. Lipowsky, *Phys. Rev. B* **28**:5273 (1983).
15. J. D. Van der Waals, *Z. Phys. Chem.* **13**:657 (1894).
16. N. G. Van Kampen, *Phys. Rev.* **135A**:362 (1964).
17. J. K. Percus, *Trans. N. Y. Acad. Sci.* **26**:1062 (1964).
18. D. E. Sullivan, *Phys. Rev. B* **20**:3991 (1979).
19. T. Aukrust and E. H. Hauge, *Phys. Rev. Lett.* **54**:1814 (1985).
20. E. Brezin, B. Halperin, and S. Leibler, *Phys. Rev. Lett.* **50**:1387 (1983).
21. S. Dietrich and M. Schick, *Phys. Rev. B* **33**:4952 (1986).
22. M. Napiorkowski and S. Dietrich, *Phys. Rev. B* **34**:6469 (1986).
23. V. Privman, *J. Chem. Phys.* **81**:2463 (1984).
24. P. Tarazona and R. Evans, *Mod. Phys.* **47**:1033 (1982).
25. J. P. Henderson, *Mol. Phys.* **59**:1049 (1986).
26. K. Binder, D. P. Landau, and D. M. Kroll, *Phys. Rev. Lett.* **56**:2272 (1986).
27. S. Nordholm, M. Johnson, and B. C. Freasier, *Aust. J. Chem.* **33**:2139 (1980).
28. J. K. Percus, *J. Chem. Phys.* **75**:1316 (1981).
29. J. K. Percus and G. O. Williams, *J. Chem. Phys.* **79**:3009 (1983).
30. T. F. Meister and D. M. Kroll, *Phys. Rev. A* **31**:4655 (1985).
31. J. K. Percus, *J. Stat. Phys.* **15**:505 (1976).
32. J. K. Percus, in *Liquid State of Matter*, E. W. Montroll and J. L. Lebowitz, eds. (1982).
33. J. K. Percus and G. O. Williams, in *Fluid Interfacial Phenomena*, C. A. Croxton, ed. (Wiley, 1986).