Cratering due to surface defects in the Gaussian model[a]

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Surface defects on freshly applied liquid films like the phenomenon of cratering are characterized by almost discontinuous interfacial profiles. Our purpose is to model the effect of surface inhomogeneities and impurities that influence the equilibrium configuration of the surface film. We therefore employ the Gaussian model which is known to provide a simple equilibrium statistical thermodynamics description of the liquid–vapor interface. By modifying previous work by Weeks, we allow for additional external forces acting on the interface and discuss the resulting shape of the surface profile. Even local application of external forces leads to deviation from the plane surface decaying on a macroscopic length scale. This does not accurately model the cratering phenomenon. In systems, which can be described by our Gaussian model, surface tension forces will always lead to a smooth interfacial profile.

I. INTRODUCTION

Surface defects of freshly applied liquid films are a familiar problem; for instance, in paint technology. One of these defects is the phenomenon of cratering, which is characterized by scattered depressions in the film surface.[1] The present work was initiated by the question of whether such well-localized depressions and the almost steplike behavior of the surface profile can be explained in the framework of a simple equilibrium statistical thermodynamics model.

Our calculations are based on a discussion of the structure and the thermodynamics of the liquid vapor interface by Weeks,[2] who employed a so-called continuous (or unweighted) Gaussian model. In this model, the entire volume is divided into an array of columns whose width l is of the order of the bulk correlation length. Changes in the number of particles in a particular column are related to changes in the local Gibbs surface. The free energy associated with such distortions of the Gibbs surface can be expressed in terms of the occupation numbers of the columns including effects of surface tension and gravity.

In this paper, we shall discuss the effect of additional external forces acting on the interface. Our purpose is to model the effect of surface inhomogeneities or impurities that influence the equilibrium configuration of the surface film. For instance, one might think of electromagnetic forces on a surface covered by charges or a dipole layer due to charged impurities.

We therefore allow for contributions from an additional potential in the expression for the free energy. For sufficiently small deviations from a planar interface, this potential energy can be linearized in these deviations and we obtain what we will call a modified Gaussian model. It is presented in detail in the next section. In Sec. III we give some examples discussing particular forms of the external forces.

Since one might feel that a model using only the linear terms in the external potential is more appropriate for discussing small perturbations of a plane interface than a phenomenon like cratering, we brieffy discuss more general forms for the external potential. In Sec. IV we show that the shape of the interface calculated in a model allowing for quadratic terms in the potential exhibits the same general features as the one calculated in our modified Gaussian model.

We summarize our results in the last section which contains some conclusions for the equilibrium shape of a liquid–vapor interface subject to external forces.

II. THE MODIFIED GAUSSIAN MODEL

Our model is a modification of the model introduced by Weeks, we first briefly describe his model essentially using the notation of Ref. 2.

The particles are contained in a cube of volume L^3 and a rectangular coordinate system is located at the center of the bottom plane of the box. The whole volume V is divided into a square array of M^2 columns extending from the top to the bottom of the box. Each column has width l in both the x and y directions. There are periodic boundary conditions at the faces of the box in the x and y directions. We fix the particle number N such that the average Gibbs surface is at $Z=H$, i.e.,

$$\rho=\frac{N}{V}=\frac{H}{L}\,\rho_l+\frac{L-H}{L}\,\rho_g\,, \tag{2.1}$$

where ρ_l and ρ_g are the bulk density of the liquid phase and the coexisting vapor phase, respectively. If column i contains n_i particles we can define a corresponding position Z_i+H of the local Gibbs surface according to

$$n_i=\rho_l\,l^2(H+Z_i)+\rho_g\,l^2(L-H-Z_i)\,, \tag{2.2}$$

which yields

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$$Z_i = \left(\frac{n_i/Ll^2 - \rho_g}{\rho_l - \rho_g} - \frac{H}{L}\right)\cdot L \ . \tag{2.3}$$

As a matter of convenience we introduce a set of "height variables" (h_i) by

$$h_i = n_i - \frac{N}{M^2} = l^2(\rho_l - \rho_g)Z_i \ . \tag{2.4}$$

Weeks has shown that then the interfacial properties of the system can be described in terms of the model partition function

$$Z_0 = \sum_{(h_i)}{}' \exp\left\{-\tfrac{1}{2}\beta\Gamma\left[\sum_i\sum_\delta (h_i - h_{i+\delta})^2 + 2G^2\sum_i h_i^2\right]\right\}. \tag{2.5}$$

δ is a nearest neighbor vector to site i, and the prime on the sum signifies that the constraint

$$\sum_i h_i = 0 \tag{2.6}$$

must be obeyed since the total number of particles is fixed. In Eq. (2.5), β is the inverse of Boltzmann's constant times temperature,

$$\Gamma = \frac{\gamma}{4l^4(\rho_l - \rho_g)^2}, \tag{2.7}$$

where γ is the surface tension, and

$$G^2 = \frac{1}{\gamma}\, 2mg\, l^2(\rho_l - \rho_g), \tag{2.8}$$

where g is the gravitational constant.

For the theory to be internally consistent, the column width l should be of the order of the bulk correlation length in the liquid.

Since in most practical situations $\beta\Gamma$ and G^2 are small (e.g., for liquid argon near the triple point $\beta\Gamma \sim 10^{-3}$, $G^2 \sim 10^{-11}$) the summation over the (h_i) may be replaced by an integral. Because of the Gaussian nature of the integrand the range of integration may be extended to $\pm\infty$.

One of Weeks' main results is the existence of very long-ranged correlations parallel to the interface. If $\mathbf{S}_i$ denotes a dimensionless lattice vector in the $Z=0$ plane giving the location of the center of column i (then the distance between the centers of columns i and j is $l(|\mathbf{S}_i - \mathbf{S}_j|)$ and thermodynamic averages are denoted by brackets $\langle\cdot\cdot\rangle$ (subscript 0 refers to the system described by Z_0), he obtains

$$\langle h_i h_j\rangle_0 - \langle h_i\rangle_0\langle h_j\rangle_0 = \frac{1}{\beta\Gamma}V(\mathbf{S}_i - \mathbf{S}_j), \tag{2.9}$$

where

$$V(\mathbf{S}) = \frac{1}{2M^2}\sum_{\mathbf{q}\neq 0}\frac{\exp\{i\mathbf{q}\cdot\mathbf{S}\}}{4 - 2\cos q_x - 2\cos q_y + G^2}\ . \tag{2.10}$$

The reciprocal lattice vectors $\mathbf{q}$ obey the constraints

$$q_x = (2\pi/M)a, \quad -\tfrac{1}{2}M \le a < \tfrac{1}{2}M,$$

$$q_y = (2\pi/M)b, \quad -\tfrac{1}{2}M \le b < \tfrac{1}{2}M,$$

where a and b are integers.

Weeks has shown that in the thermodynamic limit $(L\to\infty)$ a good approximation for $V(\mathbf{S})$ is given by

$$V(\mathbf{S}) \approx \frac{1}{4\pi}\int_0^\pi dq\, \frac{q}{q^2 + G^2} J_0(qS) \tag{2.11}$$

$$\approx \begin{cases} -(1/4\pi)\ln G & \text{for } S = 0\ , & (2.12)\\ (1/4\pi)K_0(GS) & \text{for } S > 0\ , & (2.13)\end{cases}$$

where J_0 and K_0 are an ordinary and a modified Bessel function, respectively. K_0 diverges logarithmically for small arguments, hence including gravity is crucial in order to get finite fluctuations.

As $K_\nu(Z) \sim e^{-Z}$ for $Z\to\infty$, correlations are very long ranged, decaying on a length scale

$$\lambda = l/G\ , \tag{2.14}$$

which is usually of the order of 1 mm.

Here our purpose is to discuss the effect of additional external forces acting on the interface. Accordingly, we modify the model described above by introducing into the partition function a contribution from an external potential energy Φ. We assume that Φ can be written as a sum of contributions from all columns

$$\Phi = \sum_i \varphi[l\mathbf{S}_i + (H + Z_i)\mathbf{e}_Z]\ , \tag{2.15}$$

where $\mathbf{e}_Z$ is the unit vector in the Z direction. If the resulting deviations from a plane interface are sufficiently small we may linearize in Z_i or h_i respectively, and obtain

$$\Phi \approx \Phi_0 + \sum_i f_i h_i\ , \tag{2.16}$$

where f_i is proportional to the force on the top of column i for the unperturbed interface. As the constant term Φ_0 is unimportant for the following considerations we may set $\Phi_0 = 0$.

The perturbed system can now be discussed in terms of the partition function of a "modified" Gaussian model

$$Z = \sum_{(h_i)}{}' \exp\left\{-\tfrac{1}{2}\beta\Gamma\left[\sum_i\sum_\delta (h_i - h_{i+\delta})^2 + 2G^2\sum_i h_i^2\right] - \beta\sum_i f_i h_i\right\}. \tag{2.17}$$

Elementary algebra, which is outlined in Appendix A, leads to

$$Z = \exp\left\{\tfrac{1}{2}\beta\Gamma\left[\sum_i\sum_\delta (T_i - T_{i+\delta})^2 + 2G^2\sum_i T_i^2\right]\right\} \times \sum_{(h_i)}{}'\exp\left\{-\tfrac{1}{2}\beta\Gamma\left[\sum_i\sum_\delta (h_i - T_i - h_{i+\delta} + T_{i+\delta})^2 + 2G^2\sum_i (h_i - T_i)^2\right]\right\}, \tag{2.18}$$

where

$$T_i = -\frac{1}{\Gamma}\frac{1}{2M^2}\sum_j\sum_{\mathbf{q}}\frac{\exp[i\mathbf{q}(\mathbf{S}_i - \mathbf{S}_j)]}{4 - 2\cos q_x - 2\cos q_y + G^2} f_j\ . \tag{2.19}$$

By introducing new variables $\bar{h}_i = h_i - T_i$, (besides a constant factor) (2.18) resembles the form of the partition function (2.5) of the original model. The constraint $\sum$ $\sum h_i = 0$ leads to

$$\sum_i \tilde{h}_i = -\frac{1}{2\Gamma G^2}\sum_i f_i \ , \tag{2.20}$$

and so it is more convenient to define variables

$$\hat{h}_i = \tilde{h}_i + \frac{1}{2M^2\Gamma G^2}\sum_j f_j$$
$$= h_i + \frac{1}{\Gamma}\sum_j V(\mathbf{S}_i - \mathbf{S}_j) f_j \ , \tag{2.21}$$

which fulfill the same constraint as the h_i:

$$Z = \exp\left\{\tfrac{1}{2}\Gamma\left[\sum_i\sum_j (T_i - T_{i+\delta})^2 + 2G^2\sum T_i^2\right]\right\}$$
$$\cdot \sum_{\{\hat{h}_i\}}{}' \exp\left\{-\tfrac{1}{2}\beta\Gamma\left[\sum_i\sum_\delta(\hat{h}_i - \hat{h}_{i+\delta})^2 + 2G^2\sum_i \hat{h}_i^2\right]\right\} \tag{2.22}$$

can be evaluated by exactly the same methods used for the calculation of Z_0. One immediately obtains $\langle \hat{h}_i\rangle = 0$ and therefore

$$\langle h_i\rangle = -\frac{1}{\Gamma}\sum_j V(\mathbf{S}_i - \mathbf{S}_j) f_j \ . \tag{2.23}$$

Quite generally, averages for the modified system can be expressed in terms of averages for the unperturbed system. As shown in Appendix B we have for any function F of the height variables h_i,

$$\langle F(\{h_i\})\rangle = \langle F(\{h_i + \langle h_i\rangle_0\})\rangle_0 \ . \tag{2.24}$$

Hence, introducing a potential energy of form (2.16) does not lead to any additional correlation, e.g.,

$$\langle h_i h_j\rangle - \langle h_i\rangle\langle h_j\rangle$$
$$= \langle h_i h_j\rangle_0 - \langle h_i\rangle_0\langle h_j\rangle_0 = \frac{1}{\beta\Gamma} V(\mathbf{S}_i - \mathbf{S}_j) \ . \tag{2.25}$$

Our result

$$\langle h_i\rangle = -\frac{1}{\Gamma}\sum_j V(\mathbf{S}_i - \mathbf{S}_j) f_j$$
$$= -\beta\sum_j\{\langle h_i h_j\rangle_0 - \langle h_i\rangle_0\langle h_j\rangle_0\} f_j \tag{2.26}$$

resembles a result from linear theory, but it is an exact and rigorous result for the model.

As the new interfacial profile is a convolution of the f_i with a correlation function of the unperturbed system, which is known to be very long ranged, even a well-localized external force will lead to a rather smooth and long ranged perturbation of the previously planar profile. For example, if $f_i = 0$ for $|\mathbf{S}_i| > d$ we obtain

$$\langle h_k\rangle = -\frac{\sum_i f_i}{4\pi\beta\Gamma}\sqrt{\frac{\pi}{2GS_k}}\exp\{-GS_k\} \quad \text{for } S_k \gg d \ . \tag{2.27}$$

The following section gives examples for interfacial profiles for special forms of the potential energy. For practical calculations it is convenient to introduce

$$\tilde{f}(\mathbf{q}) = \frac{1}{M}\sum_j f_j \exp(-i\mathbf{q}\cdot\mathbf{S}_j) \ . \tag{2.28}$$

Then,

$$f_j = \frac{1}{M}\sum_{\mathbf{q}} \tilde{f}(\mathbf{q})\exp(i\mathbf{q}\cdot\mathbf{S}_j) \ . \tag{2.29}$$

For potentials with axial symmetry $f_i = f(|\mathbf{S}_i|)$ and $\tilde{f}(\mathbf{q}) = \tilde{f}(|\mathbf{q}|)$. Using Weeks' approximation for $V(\mathbf{S})$ [Eq. (2.11)] the interfacial profile is then given, in the thermodynamic limit, by

$$\langle Z_m\rangle = -\frac{M}{\pi}\frac{l^2(\rho_l - \rho_g)}{\gamma}\int_0^\pi dq\,\frac{q}{q^2 + G^2}\tilde{f}(q) J_0(qS_m) \ . \tag{2.30}$$

III. EXAMPLES

This section involves some special functions and nontrivial integrals. For the definitions and properties of these functions the reader is referred to Gradshteyn and Ryzhik,[3] where all integrals can be found as well.

A. Quasi-one-dimensional situations

In this case, the system is translationally invariant in one direction, which we choose to be the y direction, hence,

$$f_j = f(\mathbf{S}_j) = f(S_j^{(x)}) \ , \tag{3.1}$$

and we immediately obtain from the general result (2.23),

$$\langle h_i\rangle = \langle h(S_i^{(x)})\rangle$$
$$= -\frac{1}{\Gamma}\sum_j \tilde{V}(S_i^{(x)} - S_j^{(x)}) f(S_j^{(x)}) \ , \tag{3.2}$$

where

$$\tilde{V}(S) = \frac{1}{2M}\sum_{\substack{q_x \\ q_x \neq 0}} \frac{e^{iq_x S}}{2(1-\cos q_x) + G^2} \ . \tag{3.3}$$

In the thermodynamic limit,

$$\tilde{V}(S) = \frac{1}{2\pi}\int_0^\pi dq\,\frac{\cos qS}{2(1-\cos q) + G^2}$$
$$= \frac{1}{4}\frac{\mathcal{K}}{\sqrt{1-\mathcal{K}^2}}\left(\frac{1-\sqrt{1-\mathcal{K}^2}}{\mathcal{K}}\right)^S \ , \tag{3.4}$$

where

$$\mathcal{K}^{-1} = 1 + \tfrac{1}{2}G^2 \ . \tag{3.5}$$

An asymptotic expansion[4] shows that, for large S,

$$\tilde{V}(S) \sim \frac{1}{2\pi}\int_0^\infty dq\,\frac{\cos qS}{q^2 + G^2} = \frac{1}{4G}\exp(-G|S|) \ . \tag{3.6}$$

But this exponential decay is even a good approximation, for small values of S. This can be seen by expanding the exact result (3.4),

$$\frac{\mathcal{K}}{\sqrt{1-\mathcal{K}^2}} = \frac{1}{G}[1 + O(G^2)] \ , \tag{3.7}$$

$$\frac{1-\sqrt{1-\mathcal{K}^2}}{\mathcal{K}} = 1 - G + \tfrac{1}{2}G^2 + O(G^3) \ . \tag{3.8}$$

As G is very small, we may use Eq. (3.6) for an arbitrary value of S.

In order to show how a discontinuity in the force profile affects the shape of the interface, we examine the case

$$f(S_j^{(x)}) = \begin{cases} f & \text{for } |S_j^{(x)}| \leq d \ , \\ 0 & \text{for } |S_j^{(x)}| > d \ . \end{cases} \tag{3.9}$$

Inserting Eq. (3.6) in Eq. (3.2) yields

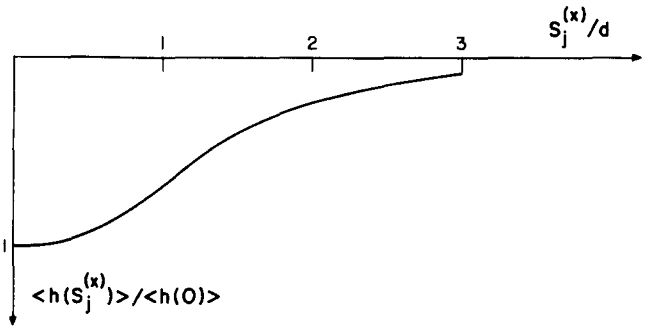

FIG. 1. Shape of the interface: quasi-one-dimensional situation with a discontinuity in the force profile at $S_j^{(x)}=d$, $Gd=1$.

$$\langle h(S_j^{(x)})\rangle = -\frac{f}{4\Gamma G^2 d}\begin{cases}1-\exp(-Gd)\cosh GS_j^{(x)} & \text{for } |S_j^{(x)}|\le d\ ,\\ \exp(-GS_j^{(x)})\sinh Gd & \text{for } |S_j^{(x)}|\ge d\ .\end{cases} \tag{3.10}$$

Regarded as a function of the continuous variable $S_j^{(x)}$, $g=\langle h(S_j^{(x)})\rangle$ and its first derivative are both continuous while there is a jump in the second derivative at the location of the jump in the force profile

$$\lim_{\epsilon\to 0+}\frac{g''(d+\epsilon)-g''(d-\epsilon)}{g''(d-\epsilon)} = -\frac{1}{2}\frac{1}{1+\exp(-2Gd)}\ . \tag{3.11}$$

A graph of g is presented in Fig. 1.

This example clearly shows that even discontinuities in the external forces still lead to a smooth surface profile. In accordance with our general results, perturbations of the planar interface are long ranged, decaying exponentially on a length scale λ [Eq. (2.14)] although the forces are extremely localized.

B. Two-dimensional situations

In order to give more realistic examples, we discuss the case of a point charge located at the bottom of the liquid layer (e.g., a charged impurity) whose electric field acts on the liquid–vapor interface.

1. Surface covered by charges

If the surface is covered by a layer of charges with surface charge density σ, the potential energy due to a point charge at the origin of the coordinate system is

$$\Phi = -\sigma l^2 Q\sum_i \{l^2 S_i^2 + (H+Z_i)^2\}^{-1/2}\ . \tag{3.12}$$

Linearization in Z_i leads to

$$f_i = \frac{\sigma Q \mathcal{H}}{(\rho_l-\rho_g)\,l^2}(S_i^2+\mathcal{H}^2)^{-3/2}\ , \tag{3.13}$$

where

$$\mathcal{H} = (1/l)H\ . \tag{3.14}$$

In order to find the Fourier transform $\tilde{f}_q$ we start from

$$f_j = \frac{1}{M}\sum_{\mathbf{q}}\tilde{f}(q)\exp(i\mathbf{q}\cdot\mathbf{S}_j)$$
$$\approx \frac{2\pi}{M}\int_0^\infty dq\, q\, J_0(qS_j)\,\tilde{f}(q)\ . \tag{3.15}$$

Using a result of Ref. 3, this immediately leads to

$$\tilde{f}(q) = \frac{2\pi}{M}\,\frac{\sigma Q}{\rho_l-\rho_g}\,\frac{1}{l^2}\exp\{-\mathcal{H}q\}. \tag{3.16}$$

To calculate the surface profile, we must evaluate

$$\frac{\langle Z_m\rangle}{H} = -2\alpha\int_0^\infty dq\,\frac{q}{q^2+G^2}\exp\{-\mathcal{H}q\}\,J_0(qS_m)\ , \tag{3.17}$$

where α is the ratio

$$\alpha = \frac{(\sigma l^2 Q/H)}{\gamma l^2}\ , \tag{3.18}$$

which is a measure of the strength of the electromagnetic compared to surface tension forces.

The result for $S_m=0$ can be given in terms of sine and cosine integrals

$$\frac{1}{H}\langle Z_0\rangle = 2\alpha\{\mathrm{ci}(G\mathcal{H})\cos(G\mathcal{H})+\mathrm{si}(G\mathcal{H})\sin(G\mathcal{H})\}$$
$$\approx 2\alpha\ln G\mathcal{H} = 2\alpha\ln\frac{H}{\lambda}\ ,\quad \text{for } G\mathcal{H}\ll 1\ . \tag{3.19}$$

The case of small S_m (i.e., $S_m G \ll 1$) can be treated by regarding $W(S_m)=(1/H)\langle Z_m\rangle$ as a function of the continuous variable S_m and approximating the derivative

$$W'(S_m) = \frac{2\alpha}{S_m}\int_0^\infty dq\exp\left\{-\frac{\mathcal{H}}{S_m}q\right\}J_1(q)\left(1-\frac{S_m^2G^2}{q^2+S_m^2G^2}\right)$$
$$\approx \frac{2\alpha}{S_m}\int_0^\infty dq\exp\left\{-\frac{\mathcal{H}}{S_m}q\right\}J_1(q)$$
$$= \frac{2\alpha}{S_m}\left(1-\frac{\mathcal{H}}{\sqrt{S_m^2+\mathcal{H}^2}}\right)\ . \tag{3.20}$$

Elementary integration yields

$$\frac{1}{H}(\langle Z_m\rangle - \langle Z_0\rangle) = 2\alpha\ln\{\tfrac{1}{2}(1+\sqrt{1+S_m^2/\mathcal{H}^2})\}\ . \tag{3.21}$$

The asymptotic behavior for $S_m \gg \mathcal{H}$ can also easily be calculated

$$\frac{1}{H}\langle Z_m\rangle = -2\alpha\int_0^\infty dq\,\frac{q}{q^2+G^2S_m^2}\exp\left(-\frac{\mathcal{H}}{S_m}q\right)J_0(q)$$
$$\approx -2\alpha\int_0^\infty dq\,\frac{q}{q^2+G^2S_m^2}J_0(q) = -2\alpha K_0(GS_m)\ . \tag{3.22}$$

An analytic expression for $\langle Z_m\rangle$, which is valid for all values of S_m can be given in the limiting case of a very shallow liquid layer, i.e., $\mathcal{H}G = H/\lambda \ll 1$, as

$$W'(S_m) = \frac{2\alpha}{S_m}\left\{\int_0^\infty dq\exp\left(-\frac{\mathcal{H}}{S_m}q\right)J_1(q) - G\int_0^\infty dq\,\frac{1}{q^2+1}J_1(qGS_m)\exp(-\mathcal{H}G_q)\right\}$$
$$\approx \frac{2\alpha}{S_m}\left\{\int_0^\infty dq\exp\left(-\frac{\mathcal{H}}{S_m}q\right)J_1(q) - G\int_0^\infty dq\,\frac{1}{q^2+1}J_1(qGS_m)\right\} = 2\alpha\left\{GK_1(GS_m)-\frac{1}{S_m}\sqrt{S_m^2+\mathcal{H}^2}\right\}\ , \tag{3.23}$$

which yields

$$\frac{1}{H}\langle Z_m\rangle = 2\alpha\{\ln(G\mathcal{K}) + \ln[\tfrac{1}{2}(1+\sqrt{\ \ +S_m^2/\mathcal{K}^2})] - \ln(\tfrac{1}{2}GS_m) - K_0(GS_m)\} = 2\alpha\ \ln(1+\sqrt{1}+S_m^2/\mathcal{K}^2) - \ln(S_m/\mathcal{K}) - K_0(GS_m)\}. \qquad (3.24)$$

A graph of this function, is presented in Fig. 2. The surface profile is well behaved, smooth and deviations from the plane interface are long ranged.

2. Surface covered by a dipole layer

Next we discuss the case of the point charge acting on a surfaee covered by a dipole layer. Denoting the surface dipole density by μ and assuming that the dipoles orient parallel to the electric field, the potential energy is

$$\Phi = -\mu l^2 Q \sum_i \{l^2 S_i^2 + (H+Z_i)^2\}^{-1}, \qquad (3.25)$$

hence,

$$f_i = \frac{2\mu Q\mathcal{K}}{(\rho_l - \rho_g)l^3}(S_m^2 + \mathcal{K}^2)^{-2}, \qquad (3.26)$$

which leads to

$$\tilde{f}(q) = \frac{2\pi}{M}\frac{\mu Q}{(\rho_l - \rho_g)l^3} qK_1(\mathcal{K}q) \qquad (3.27)$$

and

$$\frac{\langle Z_m\rangle}{H} = -2\tilde{\alpha}\int_0^\infty dq\,\frac{q^2}{q^2+G^2}K_1(\mathcal{K}q)J_0(qS_m). \qquad (3.28)$$

The ratio

$$\tilde{\alpha} = \frac{\mu l^2 Q^2}{H^2}\Big/\gamma l^2 \qquad (3.29)$$

is again a measure of the relative strength of electromagnetic and surface tension forces.

Z_0 can be expressed in terms of the Lommel's function $S_{-2,1}$:

$$\frac{\langle Z_0\rangle}{H} = -2\tilde{\alpha}GS_{-2,1}(G\mathcal{K})$$

$$\approx -2\tilde{\alpha}\frac{1}{\mathcal{K}}\ln(\tfrac{1}{2}G\mathcal{K}) \quad \text{for } G\mathcal{K} \ll 1. \qquad (3.30)$$

By analysis completely analogous to the one used in the preceding example, we obtain

$$\frac{1}{H}(\langle Z_m\rangle - \langle Z_0\rangle) = \frac{\tilde{\alpha}}{\mathcal{K}}\ln\left(1+\frac{S_m^2}{\mathcal{K}^2}\right) \quad \text{for } S_m G \ll 1, \qquad (3.31)$$

$$\frac{1}{H}\langle Z_m\rangle = \frac{2\tilde{\alpha}}{\mathcal{K}}K_0(GS_m) \quad \text{for } S_m \gg \mathcal{K}. \qquad (3.32)$$

For the limiting case of a very shallow film, i.e., for $\mathcal{K}G = H/\lambda \ll 1$,

$$\frac{1}{H}\langle Z_m\rangle = \frac{2\tilde{\alpha}}{\mathcal{K}}\left\{\ln\sqrt{1+\frac{S_m^2}{\mathcal{K}^2}} - \ln\frac{S_m}{\mathcal{K}} - K_0(GS_m)\right\}. \qquad (3.33)$$

The general properties of the profile, which is depicted in Fig. 3, are very similar to the one discussed before. Due to the stronger decay of the forces in the dipole case, deviations from the plane interface decay faster: for $S_m \gg \mathcal{K}$ we get a leading term $\sim(\mathcal{K}/S_m)^2$ in Eq. (3.33) compared to a leading term $\sim(\mathcal{K}/S_m)$ in Eq. (3.24).

IV. OTHER FORMS OF THE EXTERNAL POTENTIAL

The results of the preceding sections show that our modified Gaussian model always yields a smooth shape of the interface and therfore cannot accurately describe the cratering phenomenon. One might think that this is a consequence of our approximation (2.16) for the external potential, which includes only the terms linear in the (h_i), and that using a potential of the form

$$\Phi = \Phi(\{h_{i0}\}) + \frac{1}{2}\sum_i k_i(h_i - h_{i0})^2, \quad k_i \geq 0 \qquad (4.1)$$

would be more appropriate. In order to model a cratering defect, one would choose the h_{i0}, which clearly represent the minimum in Φ, so that they correspond to a film thickness much less than the average thickness in the region where the impurities are located. In addition, one has to take the k_i sufficiently large at impurity sites, while $k_i = 0$ at all other sites.

We, therefore, discuss the model partition function

$$Z = \exp\left\{-\beta\left(\sum_{i,j} h_i M_{ij} h_j + \sum_j f_j h_j\right)\right\}, \qquad (4.2)$$

where

$$\mathbf{M} = \mathbf{M}^{(0)} + \mathbf{M}^{(1)}, \qquad (4.3)$$

$$\mathbf{M}_{ij}^{(0)} = (4\Gamma + G^2\Gamma)\delta_{ij} - G\Gamma\sum_{\substack{\delta\\(vv)}}\delta_{i-j,\delta}, \qquad (4.4)$$

$$M_{ij}^{(1)} = \tfrac{1}{2}k_i\delta_{ij}, \qquad (4.5)$$

$$f_j = -k_j h_{j0}, \qquad (4.6)$$

and again an irrelevant constant term in Φ has been dropped.

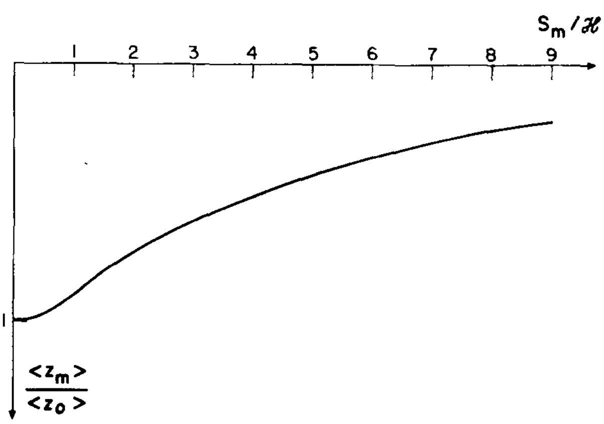

FIG. 2. Shape of the interface: surface covered by charges in the field of a point charge, $\mathcal{K}G = 0.1$.

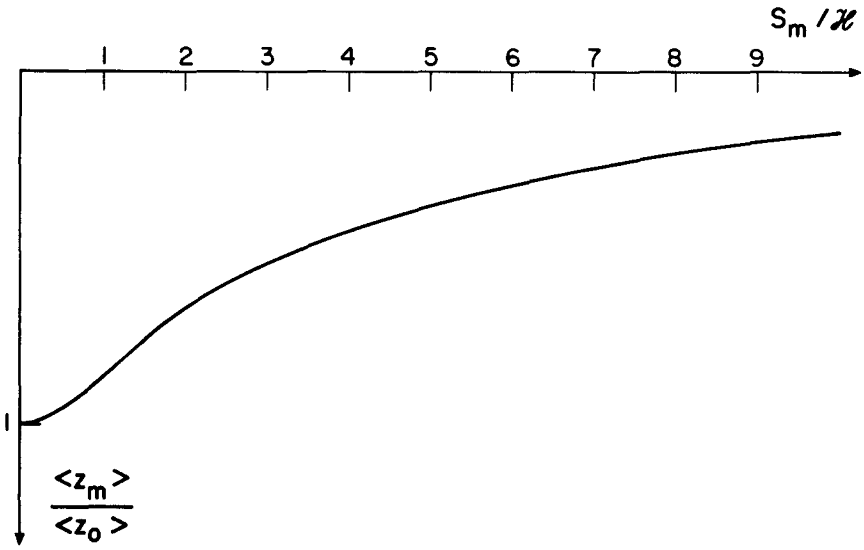

FIG. 3. Shape of the interface: surface covered by a dipole layer in the field of a point charge $\mathcal{H}G = 0.1$.

By an elementary calculation analogous to the one in Appendix A, one obtains

$$\langle h_i \rangle = -\frac{1}{2}\sum_j (\mathbf{M}^{-1})_{ij} f_j \,, \tag{4.7}$$

and hence

$$\langle h_i h_j \rangle - \langle h_i \rangle \langle h_j \rangle = -\frac{1}{\beta}\frac{\partial}{\partial f_j}\langle h_i \rangle = \frac{1}{2\beta}(\mathbf{M}^{-1})_{ij} \,. \tag{4.8}$$

So the matrix $\mathbf{M}^{-1}$ is the quantity of main interest. As $\mathbf{M}^{(0)^{-1}}$ is known, i.e.,

$$(\mathbf{M}^{(0)^{-1}})_{ij} = \frac{2}{\Gamma} V(\mathbf{S}_i - \mathbf{S}_j) \,, \tag{4.9}$$

it is convenient to write $\mathbf{M}^{-1}$ as

$$\mathbf{M}^{-1} = \mathbf{M}^{(0)^{-1}} - \mathbf{M}^{(0)^{-1}}\,\mathbf{T}\,\mathbf{M}^{(0)^{-1}} \,, \tag{4.10}$$

where we have introduced the "T matrix"

$$\mathbf{T} = (1 + \mathbf{M}^{(1)}\mathbf{M}^{(0)^{-1}})^{-1}\,\mathbf{M}^{(1)} \,. \tag{4.11}$$

$M_{ij}^{(1)}$ and therefore T_{ij} are only different from zero if i and j refer to sites where an impurity is located. Hence, when writing Eq. (4.7) in the form

$$\langle h_i \rangle = -\frac{1}{2}\sum_j (\mathbf{M}^{(0)^{-1}})_{ij}\,\tilde{f}_j = -\frac{1}{\Gamma}\sum_j V(\mathbf{S}_i - \mathbf{S}_j)\,\tilde{f}_j \,, \tag{4.12}$$

where

$$\tilde{f}_j = f_j - \sum_{j',j''} T_{jj'}(\mathbf{M}^{(0)^{-1}})_{j'j''} f_{j''} \,, \tag{4.13}$$

the "effective forces" $\tilde{f}_j$ like the f_j are only nonzero if j refers to an impurity site. So, the result for the shape of the interface [Eq. (4.12)] has exactly the same form as the result for the modified Gaussian model equation (2.83). It is a convolution of the very long-ranged function $V(\mathbf{S}_i - \mathbf{S}_j)$ with the "forces" (f_j), which are localized at the impurity sites. So again, the resulting interfacial profile will always be very smooth: choosing a potential energy of the form (4.1) will not lead to a considerably more accurate description of cratering. For further explanation, we give the results for the case of a single impurity site:

$$M_{ij}^{(1)} = \tfrac{1}{2} k \delta_{i,j}\,\delta_{i,0} \,. \tag{4.14}$$

Then,

$$T_{ij} = \frac{(1/2)k}{1 + (1/2)k(\mathbf{M}^{(0)^{-1}})_{00}}\,\delta_{i,j}\,\delta_{i,0} \,, \tag{4.15}$$

and using Eq. (2.12), we obtain

$$\langle h_j \rangle = V(\mathbf{S}_j)\,\frac{k/\Gamma}{1 + k/\Gamma(1/4\pi)\ln G^{-1}}\,h_{00} \tag{4.16}$$

$$= h_{00}\,\frac{k/\Gamma\, V(\mathbf{S}_j)}{1 + k/\Gamma\, V(0)} \,, \tag{4.17}$$

and

$$\langle h_i h_j \rangle - \langle h_i \rangle \langle h_j \rangle = \frac{1}{\beta\Gamma}\left\{ V(\mathbf{S}_i - \mathbf{S}_j) - \frac{k/\Gamma}{1 + k/\Gamma\, V(0)}\, V(\mathbf{S}_i) V(\mathbf{S}_j) \right\}. \tag{4.18}$$

We note that only in the limit $k/\Gamma \gg 1$ we have $\langle h_0 \rangle = h_{00}$. While the shape of the interface is the same as the one calculated from a corresponding "modified Gaussian model," correlations are reduced in the vicinity of the impurity.

V. SUMMARY

We have shown how the effect of external forces acting on the liquid–vapor interface can be incorporated in an existing statistical thermodynamic treatment of the interface based on the Gaussian model.

In the modified Gaussian model presented above, the only effect of external forces is a renormalization of the position of the interface. Averages for the system subject to forces can directly be obtained from the averages of the unperturbed system by merely replacing the height variables h_i by $h_i - \langle h_i \rangle$.

The new interfacial profile is given by a convolution of the external forces with a correlation function of the unperturbed system. Due to the long range of this function, even local application of external forces results in deviations from the plane surface decaying on a macroscopic length scale. Physically this results from the surface tension forces which smooth even discontinuities in the force profile, thus establishing a smooth shape for the perturbed surface. These properties of the interfacial profile can also be found in another type of model allowing for quadratic terms in the potential. The Guassian model, which has proven to provide an appropriate description of the liquid–vapor interface, does not accurately describe the cratering phenomenon where apparently discontinuous surface layer profiles result from impurities.

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APPENDIX A

Define

$$H_0(\{h_i\}) = \tfrac{1}{2}\Gamma\sum_i\sum_\delta (h_i - h_{i+\delta})^2 + \Gamma G^2\sum_i h_i^2$$

$$= (4\Gamma + G^2\Gamma)\sum_i h_i^2 - \Gamma G\sum_i\sum_\delta h_i h_{i+\delta} . \qquad (A1)$$

Then

$$H_0(\{h_i - T_i\}) = (4\Gamma + G^2\Gamma)\sum_i h_i^2 - \Gamma\sum_i\sum_\delta h_i h_{i+\delta} + \sum_i h_i\left\{-2(4\Gamma + G^2\Gamma)T_i + 2\Gamma\sum_\delta T_{i+\delta}\right\} + \sum_i T_i\left\{(4\Gamma + G^2\Gamma)T_i - \Gamma\sum_\delta T_{i+\delta}\right\} , \qquad (A2)$$

differs from

$$H(\{h_i\}) = H_0(\{h_i\}) + \sum_i f_i h_i \qquad (A3)$$

only by a constant if

$$f_i = 2\Gamma\left\{\sum_\delta T_{i+\delta} - (4 + G^2)T_i\right\} . \qquad (A4)$$

This relation can easily be inverted by Fourier transformation with the result

$$T_i = -\frac{1}{\Gamma}\frac{1}{2M^2}\sum_j\sum_q \frac{\exp[i\mathbf{q}\cdot(\mathbf{S}_i - \mathbf{S}_j)]}{4 - 2\cos q_x - 2\cos q_y + G^2} f_j . \qquad (A5)$$

APPENDIX B

The average value $\langle F\rangle$ of a function F of the height variables is defined by

$$\langle F\rangle = \int d\{h_i\} p(\{h_i\}) F(\{h_i\}) , \qquad (B1)$$

where

$$p(\{h_i\}) = (1/Z)\exp\{-\beta H(\{h_i\})\} . \qquad (B2)$$

Using the results of Appendix A,

$$H(\{h_i\}) = H_0(\{h_i - T_i\}) - \sum_i T_i\left((4\Gamma + G^2\Gamma)T_i - \Gamma\sum_j T_{i+\delta}\right) \qquad (B3)$$

and

$$Z = \exp\left\{\beta\sum_i T_i\left((4\Gamma + G^2\Gamma)T_i - \Gamma\sum_\delta T_{i+\delta}\right)\right\} \cdot \int_{-\infty}^{\infty} d\{h_i\}\exp\{-\beta H_0(\{h_i - T_i\})\} \qquad (B4)$$

$$= \exp\left\{\beta\sum_i T_i\ (4\Gamma + G^2\Gamma)T_i - \Gamma\sum_\delta T_{i+\delta}\right)\right\}\cdot Z_0 .$$

Hence,

$$p(\{h_i\}) = \frac{1}{Z_0}\exp\{-\beta H_0(\{h_i - T_i\}) = p_0(\{h_i - T_i\}) \qquad (B5)$$

and

$$\langle F(\{h_i\})\rangle = \langle F(\{h_i + T_i\})\rangle_0 . \qquad (B6)$$

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