On the Thermodynamics of Nonuniform Systems

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Two methods are presented for the treatment of the nonuniform systems. Both have as a starting point the approximation of the real system by a succession of uniform systems (cells). In one of them, the nonuniformity is taken into account by attributing a free energy to the separating surfaces between the cells, while in the other by considering that the cells are under the action of an "external field" created by the nonuniformity.

A distinction between small and large nonuniform systems is made by comparing the thickness of the nonuniform system with the length of the interval in which the nonuniformity is decaying. For small systems the intensive properties depend on the thickness of the system and thus some supplementary effects, as for instance the disjoining pressure, occur.

An expression for the "external field" based on the formalism of the radial distribution function is proposed.

A large number of phenomena, such as surface tension, adsorption, disjoining pressure, nucleation, the vapor pressure of a liquid imbibing a porous medium, the influence of a solid surface upon a chemical reaction, are treated in a unitary manner by means of the present approaches.

Some previous equations such as those of Cahn-Hilliard and of Hill are derived in a different manner or justified.

The objections raised by Widom against the continuous approaches are discussed.

In some thermodynamic systems, several intensive parameters may change their values from point to point. Such systems are nonuniform. The causes and the consequences of the nonuniformity are various, such as those from the following examples:

The interfacial zone between the liquid and the vapor phases is a nonuniform system because the bulk phases have very different densities and thus the molecular forces acting upon the molecules near the interface are asymmetrical. The consequence of this nonuniformity is the surface tension. When a gas or a liquid is in contact with a solid surface, the nonuniformity is due to the interaction between the solid and the fluid. The result is the adsorption phenomenon. In an undercooled vapor phase, some large density fluctuation occurs; a system created by density fluctuation is nonuniform. If the fluctuation is sufficiently large, the nonuniform system so created is able to grow and to develop a new phase. If in the vapor phase there exists a small solid impurity, the work needed to create a nonuniform system (a fluctuation) able to develop a new phase is smaller than when the impurity is lacking. Nonuniform systems arise also when a liquid is introduced into the very small pores of a solid or when a very thin liquid film is located between two solid plates. The nonuniformity leads to a change of the vapor pressure in the first case, and in the second, to the occurrence of the disjoining pressure which tends to move away the plates.

All the above systems differ both as to the way in which the nonuniformity is created and as to the physical effects which are generated by it, but are characterized by a continuous variation of the density from point to point. A thermodynamic treatment which takes into account this variation may be called thermodynamics of nonuniform systems. Such continuous treatments have been developed by Tolman (*1*) and by Hill and Plessner (*2* to *5*) for surface tension, by Cahn and Hilliard (*6*, *7*) and Hart (*8* to *11*) for surface tension, homogeneous nucleation, and for the properties of the systems near the critical point; the connection between Cahn-Hilliard and Hart's theories was discussed by Cahn (*12*).

In Tolman's continuous method for the surface tension (*1*), the nonuniformity is taken into account by means of a supplementary potential. Usual thermodynamical manipulation is used to obtain information about the system.

The starting point of Hill's method (*2*, *3*) is the hydrostatical approach, that is the equation

$$\gamma = \int_0^\infty (p_t - p_0)\, dz$$

He considers that the tangential pressure satisfies a van der Waals equation modified to take into account the nonuniformity of the system.

The method used by Cahn and Hilliard (*7*, *8*) is based on two assumptions: (1) in a nonuniform system there exists a local density of the free energy and (2) the free energy density contains a term proportional to the square of the density gradient. The equilibrium condition leads to an equation for the dependence of the density on the distance; the equation contains a constant which must be calculated by means of a statistical model.

Widom (*13*) notices that in all the continuous approaches one must use for the density the equation of state in a range of density in which the stability condition $(\partial p/\partial V)_T < 0$, imposed by the thermodynamics of the uniform systems, is not satisfied. He used an approach based on the fluctuation theory where the above difficulty is avoided.

Our first comment concerning the above-mentioned methods is that they are highly specific. Hill's and Tolman's methods are formulated for surface tension and that of Widom for the states near the critical point, while that of Cahn and Hilliard is for surface tension, homogeneous nucleation, and the properties of a liquid near the critical point.

The aim of this paper is to develop unitary methods able to be used for a large class of phenomena in which nonuniform systems are arising.

THE THERMODYNAMIC DESCRIPTION

In order to apply to a nonuniform system the usual thermodynamic way of reasoning, we shall divide it into a sequence of small uniform systems (cells). We shall consider in the following, for simplicity, only plane systems. The walls of the cells are planes parallel to the plane interface (Figure 1). The density in the cells will be selected so as to approximate the real density of the system. Since the nonuniform system is in equilibrium, an equilibrium between the successive uniform cells must be imposed. Their equilibrium may be achieved in one of the following two ways: (1) Assigning to the dividing surfaces between the cells i and $i+1$ a free energy $\varepsilon_i A$ preventing the flow and the diffusion of the material through it. (2) Considering that the prevention of the flow and diffusion is due to an "external field" φ_i acting on a molecule from the cell and generated by the nonuniformity existing in its vicinity.

By developing these two ways to reach equilibrium, two approaches of the nonuniform systems result. The first approach is a new one. The second treatment is similar to that of Tolman (*1*) in what concerns the way in which the nonuniformity is taken into account. However, it differs from that of Tolman in two respects: it is extended here to other phenomena too (such as adsorption, nucleation, disjoining pressure, etc.); a concrete form of the field, based on the radial function formalism is proposed. The equations obtained in this way for the free energy allow one to obtain Cahn and Hilliard's results or to justify Hill's equation.

Compared to the other approaches the present ones allow a more unitary treatment of a large number of phenomena.

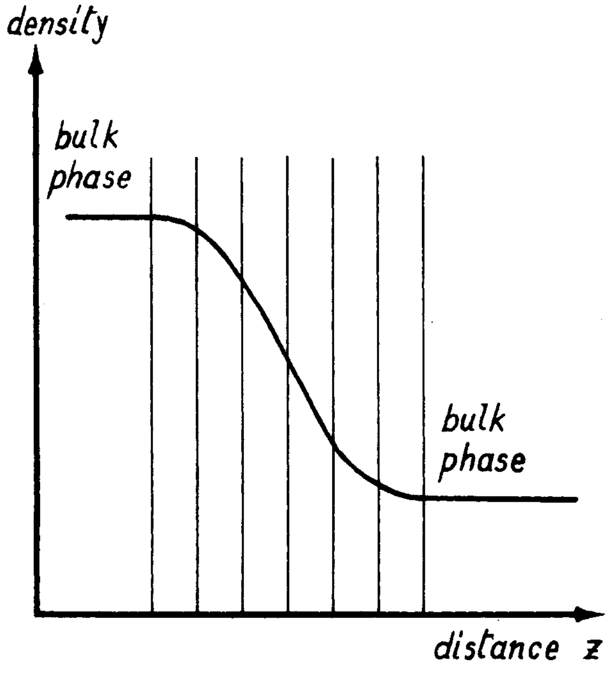

Fig. 1. The cells in the nonuniform plane systems.

It must be stressed that a continuous treatment is strictly valid only if the thickness of the nonuniform region is sufficiently large. Such a condition is, for instance, satisfied near the critical point. However some qualitative conclusions may be drawn from a continuous treatment even if the nonuniform region is a few angstroms thick.

THE FIRST APPROACH

The Thermodynamic Equations

Let us consider a nonuniform system having a thickness d. In order to analyze it from a thermodynamical point of view, let us divide the system into a number of cells, isolate two succesive cells, and assume a virtual change which keeps their total volume, entropy, and number of molecules constant.

$$\delta V_i + \delta V_{i+1} = \delta S_i + \delta S_{i+1} = \delta N_i + \delta N_{i+1} = 0 \qquad (1)$$

The thermodynamic equilibrium between the two cells is attained if under a change satisfying the constraints (1), the total energy is constant ($\delta E = 0$).

The variation of the total energy for a constant value of the area A may be written as

$$\delta E = \delta E_i + \delta E_{i+1} + A\,\delta\,\varepsilon_i \qquad (2)$$

where the supplementary term $A\,\delta\varepsilon_i$ was introduced owing to the fact that the variation of the inner state of the cells must be accompanied by a corresponding variation in the "state" of the dividing surface.

The change of state of the dividing surface depends on δV_i and δN_i, which characterize the change of the state in the cells. One can therefore write

$$\delta\varepsilon_i = \left(\frac{\partial\varepsilon_i}{\partial z_i}\right)_{N_i}\left(\frac{\partial z_i}{\partial V_i}\right)\delta V_i + \left(\frac{\partial\varepsilon_i}{\partial N_i}\right)_{V_i}\delta N_i \qquad (3)$$

Since $\delta E_i = -p_i\delta V_i + T_i\delta S_i + \mu_i\delta N_i$, taking into account also Equation (3), Equation (2) becomes

$$\delta E = -p_i\delta V_i + T_i\delta S_i + \mu_i\delta N_i - p_{i+1}\delta V_{i+1} + T_{i+1}\delta S_{i+1}$$
$$+ \mu_{i+1}\delta N_{i+1} + \left(\frac{\partial\varepsilon_i}{\partial z_i}\right)_{N_i}\delta V_i + A\left(\frac{\partial\varepsilon_i}{\partial N_i}\right)_{V_i}\delta N_i \qquad (4)$$

The two cells are in mechanical equilibrium if $\delta E = \delta N_i = \delta N_{i+1} = \delta S_i = \delta S_{i+1} = 0$ and $\delta V_i = -\delta V_{i+1}$. One obtains

$$p_{i+1} - p_i + \left(\frac{\partial\varepsilon_i}{\partial z_i}\right)_{N_i} = 0$$

For an uniform system, p_i equals p_{i+1} and $(\partial\varepsilon_i/\partial z_i)_{N_i} = 0$; hence the nonuniformity is taken into account by means of

$$(\partial\varepsilon_i/\partial z_i)_{N_i} \neq 0$$

In an analogous manner, one obtains the condition of diffusional equilibrium:

$$A\left(\frac{\partial\varepsilon_i}{\partial N_i}\right)_{V_i} = \mu_i - \mu_{i+1}$$

where $A(\partial\varepsilon_i/\partial N_i)_{V_i} \neq 0$ is a consequence of the nonuniformity.

Let us now consider the whole sequence of cells which approximate the nonuniform system. The total energy of such a system is given by

$$\delta E = \sum_i [\delta E_i + \delta(A\varepsilon_i)] = \sum_i \left\{-\left[p_i - \left(\frac{\partial\varepsilon_i}{\partial z_i}\right)_{N_i}\right]\delta V_i \right.$$
$$\left. + T\delta S_i + \left[\mu_i + A\left(\frac{\partial\varepsilon_i}{\partial N_i}\right)_{V_i}\right]\delta N_i + \varepsilon_i\delta A\right\} \qquad (5)$$

which may be written as

$$\delta E = -\bar{p}\,\delta\mathcal{V} + T\delta S + \bar{\mu}\,\delta\mathcal{N} + \eta\,\delta A \tag{6}$$

where

$$-\bar{p} \equiv .\frac{1}{d}\int_0^d \left[\left(\frac{\partial\varepsilon}{\partial z}\right)_N - p\right] dz \quad \mathcal{V} \equiv Ad \tag{7}$$

$$\bar{\mu}\mathcal{N} \equiv A\int_0^d \left[\mu + \left(\frac{\partial\varepsilon}{\partial N}\right)_V A\right] dz \quad \mathcal{N} \equiv \int_0^d n\,dz \tag{8}$$

$$\delta S \equiv \sum_i \delta S_i \tag{9}$$

$$\eta \equiv \frac{1}{d}\int_0^d \varepsilon\,dz \tag{10}$$

The variation of the excess energy with respect to uniform system is given by

$$\delta E_{\text{ex}} = (p_0 - \bar{p})\,\delta\mathcal{V} + (\bar{\mu} - \mu_0)\,\delta\mathcal{N} + \eta\,\delta A \tag{11}$$

δE_{ex} represents a global consequence of the nonuniformity of the system.

The "Small" and "Large" Systems

Two classes of nonuniform system may exist. In one of them the nonuniform region goes over continuously into a uniform one, while in the second it consists only of a nonuniform region. For instance the interface between two bulk phases is a system of the first kind. If we consider a thin liquid film located between two parallel solid plates, both situations may occur: if the distance h between the plates is sufficiently large (Figure 2*a*), a uniform region appears in the middle of the system and the system is of the first kind; if the distance h between the plates is sufficiently small (Figure 2*b*), the system is of the second kind. In order to establish a criterion for distinguishing between the two types of systems, let us analyze in more detail the last example. The nonuniform regions in Figure 2*a* extend to those distances from the solid plates at which $\varepsilon(z)$, which characterizes the nonuniformity, becomes equal to zero. Let us denote by h^* the distance from the solid plates at which $\varepsilon(z) = 0$. For the systems of the first kind the thickness h is larger than $2h^*$, while for those of the second kind it is smaller than $2h^*$. It appears natural to call "large" and "small" the first and second kinds of systems, respectively.

It will be shown in the following that such a classification is useful since for small systems the intensive properties depend on the thickness of the system, while for large systems such dependence does not appear.†

For large systems the factors $p_0 - \bar{p}$, $\bar{\mu} - \mu_0$ and η from Equation (11) may be written as

$$\int_0^h = \int_0^{h^*} + \int_{h^*}^{h-h^*} + \int_{h-h^*}^{h} = 2\int_0^{h^*} + \int_{h^*}^{h-h^*}$$

Because ε is zero in the interval $[h^*, h - h^*]$, the second integral is zero and hence the value of the remaining integral does not depend on the thickness h, but only on h^*, which is an internal parameter.

If the system is small δE_{ex} depends on the thickness h; owing to this dependence, some physical effects appear in small systems which do not occur in large ones. Two examples are given in the following.

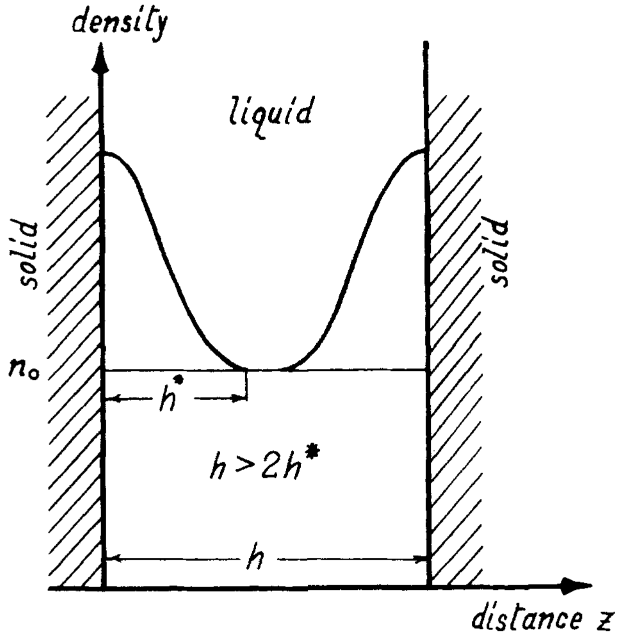

Fig. 2a. A thin liquid film between two parallel plates. The system is large because $h > 2h^*$.

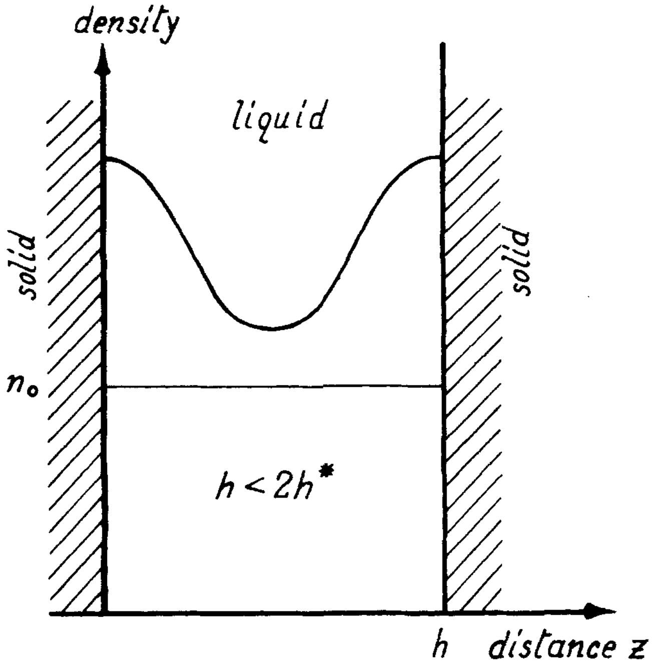

Fig. 2b. A thin liquid film between two parallel plates. The system is small because $h < 2h^*$.

The Disjoining Pressure

Let us consider a liquid film between two parallel finite plates, the film being in contact with its bulk, as in Figure 3. If $h > 2h^*$ the variation of h does not cause a change in the total energy. Consequently the condition $\delta E_t = 0$ (E_t = energy of the system between plates plus the energy of the bulk) when only h is varied, will be satisfied identically and the mechanical equilibrium is automatically achieved. If $h < 2h^*$, then the system tends to attain its equilibrium state and the plates move away until $h = 2h^*$. In order to maintain the plates at a distance $h < 2h^*$, it is necessary to act on the plates with an external pressure π. If the two plates are fixed at a distance $h < 2h^*$ then there appears on the internal sides of the plates a pressure π whose tendency is to disjoin them. The concept of disjoining pressure was

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†One may notice that the concept of smallness introduced here for the nonuniform systems is not the same as the concept of smallness introduced by Hill (*15, 16*) for uniform systems.

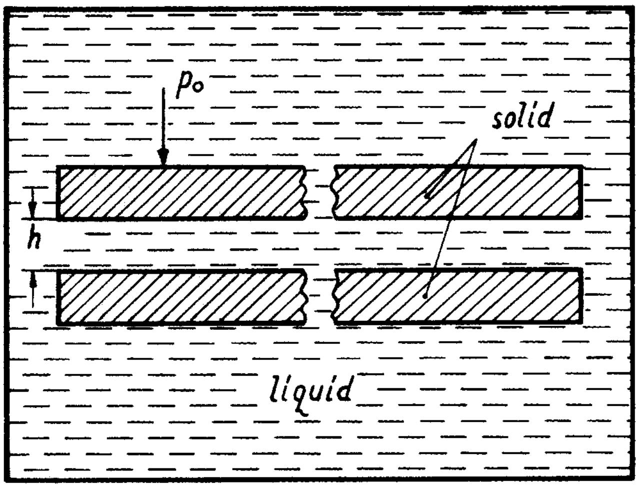

Fig. 3. A system in which disjoining pressure occurs.

first introduced by Derjaguin (*17, 18*). It is introduced here as a consequence of the thermodynamics of small nonuniform systems.

The conditions for mechanical equilibrium are in this case

$$\delta E = -\bar{p}\,\delta\mathcal{V} + T\delta S + \bar{\mu}\,\delta\mathcal{N} + \eta\,\delta A - p_0\,\delta V_0 + T\delta S_0 + \mu_0\,\delta N_0 + \pi\,\delta V_0 = 0 \tag{11a}$$

$$\delta S = \delta S_0 = \delta\mathcal{N} = \delta N_0 = \delta A = 0 \tag{11b}$$

$$\delta\mathcal{V} = -\delta V_0 = A\,\delta h \tag{11c}$$

There results

$$\pi = p_0 - \bar{p}$$

One may notice that from Equation (11) one obtains

$$\pi = \left(\frac{\partial E_{\mathrm{ex}}}{\partial\mathcal{V}}\right)_{\mathfrak{N},A} = \frac{1}{A}\left(\frac{\partial E_{\mathrm{ex}}}{\partial h}\right)_{\mathfrak{N},A}$$

As was shown in the preceding paragraph, E_{ex} depends on h if and only if the system is a small one. Consequently π is a result both of the nonuniformity and of the smallness of the system.

Using Equation (8) one obtains

$$\pi = \frac{1}{h}\int_0^h (p_0 - \mathcal{P})\,dz \tag{12a}$$

where

$$\mathcal{P} \equiv p - \left(\frac{\partial\varepsilon}{\partial z}\right)_N \tag{12b}$$

is the local pressure in the small nonuniform system. If the local pressure $\mathcal{P}$ is identified with the p_{xx} component of the stress tensor, then Equation (12*a*) is the same as the one established in a different way by Scherbakov (*18*).

The Vapor Pressure of a Liquid Imbibing a Porous Medium

Another example of the effect of smallness and nonuniformity is the change in the vapor pressure when a liquid imbibes a porous medium and the dimension of the pores is smaller than $2h^*$. The condition of the diffusional equilibrium, obtained in a similar manner as above, is

$$\bar{\mu} = \mu_0^{\mathrm{vap}}\,(T_0, p_0)$$

The above equation enables one to obtain the pressure p_0. The change of the parameters from one equilibrium state to another must satisfy the equation

$$\left(\frac{\partial\bar{\mu}}{\partial h}\right)_{\bar{p},T}\delta h + \left(\frac{\partial\bar{\mu}}{\partial\bar{p}}\right)_{T,h}\delta\bar{p} = \left(\frac{\partial\mu_0^{\mathrm{vap}}}{\partial p_0}\right)_T \delta p_0$$

where, by neglecting as usual $(\partial\bar{\mu}/\partial\bar{p})_{T_1 h}\delta\bar{p}$ as compared to $(\partial\mu_0^{\mathrm{vap}}/\partial p_0)_{\mathrm{T}}\,\delta p_0$, there results

$$\bar{\mu}(h) - \bar{\mu}(2h^*) = \int_{p_0^v}^{p_0} v_0\,dp_0$$

where p_0^v = vapor pressure of the bulk liquid and p_0 = vapor pressure when the dimension of the pores is equal to h.

If h is sufficiently close to $2h^*$ and the vapor is ideal, then

$$p_0 = p_0^v \exp\left[\left(\frac{\partial\bar{\mu}}{\partial h}\right)_{h=2h^*}\frac{h - 2h^*}{kT}\right] \tag{13}$$

THE SECOND APPROACH

Thermodynamic Equations

As was stressed under Thermodynamic Description, another possibility to avoid the mixing of the material from the uniform cells is to assume that each cell i is under the action of a field caused by the asymmetrical (nonuniform) distribution of the neighboring molecules and/or of an external field. The thermodynamic treatment presented is similar to that of Tolman (*1*), who used the formalism available for systems in external fields. The present treatment differs from that of Tolman in two respects. First, the field due to the nonuniformity of the system is calculated by using the formalism of the radial distribution function. On this basis, Cahn-Hilliard's equation is derived in a new manner. But the main new contribution is that the thermodynamic treatment, used by Tolman for the surface tension, is extended here to a large class of problems. A unitary treatment of numerous phenomena is proposed.

Let us denote by Φ_i the energy of a molecule from cell i due to the field caused by the nonuniformity. The fundamental thermodynamic equation for cell i becomes

$$\delta E_i = -p_i\delta V_i + T_i\delta S_i + (\mu_i + \Phi_i)\,\delta N_i \tag{14}$$

For the total energy of the closed system, formed from the nonuniform cells and the uniform (bulk) phases, one may write

$$\delta E_t = \sum_i \delta E_i - p_{01}\delta V_{01} + T_{01}\delta S_{01} + \mu_{01}\delta N_{01} - p_{02}\,\delta V_{02} + T_{02}\,\delta S_{02} + \mu_{02}\,\delta N_{02} \tag{15}$$

The conditions of diffusional equilibrium

$$\delta E_t = \delta S_i = \delta V_i = \delta S_{01} = \delta S_{02} = \delta V_{01} = \delta V_{02} = 0$$

and

$$\delta N_{01} + \delta N_{02} = -\sum_i \delta N_i$$

lead to

$$\sum_i \left[(\mu_i + \Phi_i) - \mu_{01}\right]\delta N_i + (\mu_{02} - \mu_{01})\,\delta N_{02} = 0$$

Since δN_i and δN_{02} are independent and arbitrary, there results that

$$\mu_i + \Phi_i - \mu_{01} = 0 \quad \text{for any } i$$

and

$$\mu_{01} = \mu_{02} \equiv \mu_0$$

Taking the limit for a large number of cells, one obtains

$$\mu[n(z), T_0] + \Phi(z, n(z), T_0) = \mu_0[T_0, p_0] \tag{16}$$

Equation (16) represents the starting point of the second approach. In this equation, $\mu[n(z), T]$ represents the chemical potential of a uniform system having the density equal to the local density $n(z)$ of the nonuniform system. Expressions for μ may be taken from experimental data referring to uniform systems or from statistical models. The term $\Phi[z, T, n(z)]$ will be examined in the following section.

Equation (16) gives the dependence of the density $n(z)$ of the nonuniform system on z. The distribution of the pressure in the nonuniform system results from the thermodynamic equation

$$\frac{\partial \mu[n(z), T]}{\partial p} = \frac{1}{n(z)} \tag{17}$$

Using for $n(z)$ values obtained from Equation (16), one may solve Equation (17), together with the boundary condition $p = p_0$ for $z = \infty$, to give the pressure distribution. We stress the fact that the pressure p given by Equation (17) is the real pressure since it coincides with the mechanical pressure given by the hydrostatic equilibrium. Indeed, from Equation (16) one obtains that

$$\frac{d\mu}{dz} = - \frac{d\Phi}{dz}$$

and consequently Equation (17) may be written as

$$\frac{1}{n(z)} \frac{dp}{dz} = - \frac{d\Phi}{dz}$$

which is the equation for hydrostatic equilibrium.

The Calculation of Φ

The energy Φ is a consequence of the nonuniformity. Three cases may arise:

1. Systems like those occurring for an interface between two bulk phases for which the nonuniformity is due to the asymmetry of the distribution of molecules. The potential created by this asymmetry will be denoted by φ.
2. Systems like the solid-vapor (or solid-liquid) interface for which the nonuniformity is due to the field ψ created by the interaction with the solid.
3. Systems like the nuclei in the heterogeneous nucleation. The nonuniformity is due both to a statistical fluctuation which creates a molecular asymmetry and to the field of the interaction with the solid.

In what follows expressions for φ will be given. Concerning the quantity ψ there exist in the literature numerous studies related to the adsorption phenomenon. The quantity φ may be calculated by means of the radial distribution function formalism. For the cell i we have

$$\varphi_i = \lim_{V_i \to 0} \left\{ \frac{1}{N_i} \int_{V_i} \int_{V-V_i} u(r_{12}) n(\vec{r}_1) n(\vec{r}_2)\, g(\vec{r}_1, \vec{r}_2)\, d\vec{r}_1\, d\vec{r}_2 - \frac{1}{N_i} \int_{V_i} \int_{V-V_i} u(r_{12})\, n_i^2 g_i(r_{12})\, d\vec{r}_1\, d\vec{r}_2 \right\} \tag{18}$$

where $n(r_k)$, $k = 1, 2$ represents the density in the point r_k (at the integration r_1 takes values in the cell i, while r_2 takes values in the remaining part of the system), $g(\vec{r}_1, \vec{r}_2)$ the radial distribution function of the nonuniform system, $g_i(r_{12})$ that of a uniform system having the density of the cell i, and $u(r_{12})$ the interaction energy between two molecules situated at the distance r_{12}.

Introducing the expression of φ_i into the equilibrium equation (16), one obtains an integral equation for the distribution of the density

$$\mu - \mu_0 = \psi + \lim_{V_i \to 0} \left\{ \frac{1}{N_i} \int_{V_i} \int_{V-V_i} u(r_{12})\, n(\vec{r}_1)\, n(\vec{r}_2)\, g(\vec{r}_1, \vec{r}_2)\, d\vec{r}_1\, d\vec{r}_2 - \frac{1}{N_i} \int_{V_i} \int_{V-V_i} u(r_{12})\, n_i^2 g_i(r_{12})\, d\vec{r}_1\, d\vec{r}_2 \right\} \tag{19}$$

To simplify the first integral from Equation (18) (which will be denoted in the following by I_1), we shall assume that $g(\vec{r}_1, \vec{r}_2) \approx g_i(r_{12})$. An argument for this simplification is the fact that very drastic assumptions concerning the radial distribution function lead in various statistical mechanics calculations to very near results. $n(\vec{r}_2)$ will be expanded into power series around $n(\vec{r}_1)$. The term containing the odd powers of $\vec{r}_2 - \vec{r}_1$ must be zero since the thermodynamic quantities must be invariant with respect to the inversion. Only the first two nonzero terms of the expansion will be retained. For the systems having a plane symmetry which are considered here, one may therefore write

$$I_1 = \frac{1}{N_i} \int_{V_i} \int_{V-V_i} n^2(\vec{r}_1)\, u(r_{12})\, g_i(r_{12})\, d\vec{r}_1\, d\vec{r}_2 + \frac{1}{2N_i} \int_{V_i} \int_{V-V_i} n(r_1) \left(\frac{d^2n}{dz^2} \right)_{z=z_1} (z_2 - z_1)^2\, g(r_{12})\, d\vec{r}_1\, d\vec{r}_2 \tag{20}$$

Since the integration with respect to $\vec{r}_1$ is performed in the volume V_i, which contains a uniform system of density n_i, we have $n(\vec{r}_1) = n_i$ and consequently the first integral from I_1 is the same with the second integral from Equation (18). Therefore

$$\varphi = \lim_{V_i \to 0} \times \left\{ \frac{1}{2N_i} \int_{V_i} \int_{V-V_i} n(r_1) \left(\frac{d^2n}{dz^2} \right)_{z=z_1} (z_2 - z_1)^2 g(r_{12}) d\vec{r}_1 d\vec{r}_2 \right\} \tag{21a}$$

The change of variable $\vec{r}_2 \longrightarrow \vec{r}_{12}$ allows one to write

$$\varphi = K(z) \frac{d^2n}{dz^2} \tag{21b}$$

where

$$K(z) = \frac{1}{2} \int_V (z_2 - z_1)^2\, g(r_{12})\, u(r_{12})\, d\vec{r}_{12} \tag{21c}$$

For a van der Waals liquid

$$g(r) = \begin{cases} 1 & r > r_0 \\ 0 & r \leq r_0 \end{cases} \tag{22a}$$

$$u(r) = \begin{cases} -\varepsilon (r_0/r)^6 & r > r_0 \\ \infty & r \leq r_0 \end{cases} \tag{22b}$$

and one obtains for φ the equation

$$\varphi = - \frac{2\pi\varepsilon\, r_0^5}{3} \frac{d^2n}{dz^2} \tag{22}$$

The function $K(z)$ is in this case a constant.

The equilibrium condition leads therefore to the following final equation:

$$\mu[n(z)] + K(z) \frac{d^2n}{dz^2} + \psi = \mu_0 \tag{23}$$

where $\mu[n(z)]$ represents the chemical potential of a uniform system having the density $n(z)$, μ_0 is the chemical potential of the bulk phases with which the nonuniform system is in equilibrium, and $K(z)$ is given by Equation (21*c*).

On the basis of this equation it is possible to obtain or to justify some preceding treatments of the nonuniform systems proposed by Cahn and Hilliard and by Hill.

Cahn-Hilliard's Equation

In Cahn-Hilliard's treatment one assumes that there exists a density f of the free energy so that the free energy of the system may be written under the form $F = \int_V f dV$, and that the local density of the free energy depends not only on the usual thermodynamic parameters, but also on the density gradients ∇n, $\nabla^2 n$, etc.

Expanding into a Taylor series and keeping the first terms invariant to inversion ($x \longrightarrow -x$), they write

$$f = f_0(n) + k_1 \nabla^2 n + k_2 (\nabla n)^2 \tag{24}$$

where the quantities k_1 and k_2 depend only on the density n.

Using Gauss' theorem one obtains

$$\int_V k_1 \nabla^2 n \, dV + \int_V \frac{dk_1}{dn} (\nabla n)^2 dV = \int k_1 \nabla n \, d\mathfrak{A}$$

The above equation enables one to write

$$F = \int_V f dV = \int_V \left[f_0 + \left(k_2 - \frac{dk_1}{dn} \right) (\nabla n)^2 \right] dV + \int_{\mathfrak{a}} k_1 \nabla n d\mathfrak{A}$$

For systems in which solid surfaces are absent (for example, liquid-vapor interface or homogeneous nucleation), the surface $\mathfrak{A}$ may be always selected so that $\int_{\mathfrak{a}} k_1 \nabla n d\mathfrak{A}$ will be nil.

If the system contains a solid surface (as in adsorption or heterogeneous nucleation), the surface $\mathfrak{A}$ must incorporate the solid surface on which $\nabla n \neq 0$ and consequently the above integral must be taken into account. Cahn and Hilliard have examined only the first situation.

In the following we shall prove that for the first situation our treatment is equivalent to that of Cahn-Hilliard.

The density of the free energy being given by

$$f = n \mu(z) + n \varphi(z) - p(z)$$

we may write that

$$F = \int_V [f_0 + n \varphi(z)] \, dV$$

where $f_0 = n\mu - p$. Using Equation (21*b*) for φ and Gauss' theorem, one obtains an equation of the Cahn-Hilliard form.

The second situation is solved in our treatment in a simple manner by taking into account into Equation (23) the interaction potential ψ between the molecules and the solid surface.

Hill'S Equation (*2,3,19*)

The departing point of Hill's theory for surface tension is the equation given by the hydrostatic model (*19*):

$$\gamma = \int_{-\infty}^{+\infty} (p_0 - p_z) \, dz \tag{25}$$

where p_0 is the pressure in the bulk of the two phases and $p_t(z)$ is the "tangential pressure" depending on z.

For the calculation of $p_t(z)$, Hill assumes that $p_t(z)$ satisfies the van der Waals equation

$$[p_t(z) + (n(z))^2 a] \left[\frac{1}{n(z)} - b \right] = kT \tag{26}$$

and that the chemical potential and the tangential pressure are connected by

$$\frac{\partial \mu}{\partial p_t} = \frac{1}{n(z)} \tag{27}$$

In this manner he obtains

$$\mu(z) = \mu^*(T) + kT \lg \left(\frac{kT}{b} \right) + kT \left[\lg \frac{\theta}{1-\theta} + \frac{\theta}{1-\theta} - \alpha \theta \right] \tag{28}$$

where

$$\alpha = 2a/bkT \text{ and } \theta \equiv bn(z).$$

To determine the function $n(z)$, Hill assumes that the equilibrium is achieved in each point if

$$\mu(z) = \mu_0 \tag{29}$$

Equation (29) does not lead to satisfactory results, since it gives a uniform density for the nonuniform system.[†] For this reason Hill corrects it by writing for the term $-kT\alpha\theta$ from Equation (28) the expression

$$-\alpha \theta kT = \int_V n(\vec{r}_2) \, g(r_{12}) \, u(r_{12}) \, d\vec{r}_{12}$$

instead of the usual expression

$$-\alpha \theta kT = n \int_V g(r_{12}) \, u(r_{12}) \, d\vec{r}_{12}$$

It is clear that this correction accounts for the nonuniformity and that in fact the chemical potential μ from Equation (29) is replaced by

$$\mu' = \mu + \int_V n(\vec{r}_2) g(r_{12}) \, u(r_{12}) d\vec{r}_{12} - n(\vec{r}_1) \int_V g(r_{12}) u(r_{12}) d\vec{r}_{12} \tag{30}$$

Calculations, such as that of Φ, lead to the conclusions that the difference between the two integrals in Equation (30) equals the potential φ. Hence the equilibrium equation (29) corrected as above is the same as our Equation (16).

Widom's Objections to the Continuous Approaches

Two objections have been raised by Widom (*13*) in connection with the continuous approaches: in the continuous approaches one must use the equation of state in a range containing also the instable region; the free energy of formation of a nonuniform system has in his opinion two terms, one of them, Φ_1, is proportional to the square of the density gradient, while the second, Φ_2, is equal to the free energy of formation of a fluctuation having the same volume as the nonuniform system and achieving the same density variation. Such an equation leads to disagreement with experiment for some properties near the critical point, while the use of only the second term for the free energy leads to agreement. The conclusion is that the term containing the square of the density fluctuation is superfluous and consequently all the theories based on the density gradient are erroneous.

A possible answer to the first objection is that the uniform system used for the calculation of μ is virtual and not a real one and thus it is meaningless to require its stability.[‡]

One may notice also that it is possible, at least in principle, to imagine an equation of state which has no instable range (Figure 4) but which has in the points m and n transformations of phases of the second order.

[†] Equation (29) is not correct, the correct equilibrium equation for the nonuniform system being Equation (15).

[‡] The same argument was produced by Parlange (*20*). (We are indebted to one of the referees for informing us about Parlange's paper.)

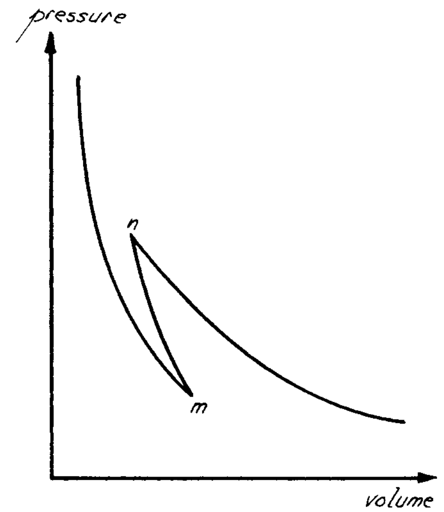

Fig. 4. A possible elimination of the unstable region from the equation of state.

As to the second objection we notice that the two terms considered represent in different "languages" the free energy of formation of the nonuniformity, and that either of them represents alone the free energy of formation of the nonuniform system. We feel that the present argument is strengthened by Widom's observation that if one uses for the dimension of the nonuniform system the correlation length from the theories of Ornstein-Zernike or Debye, then $\Phi_1 = \Phi_2$.

Because $\Phi_1 = \Phi_2$ Widom's equation for the free energy is $2\Phi_2$ instead of Φ_2; consequently his results are not essentially different.

Interfacial Tension

The interfacial tension represents the ratio between the difference of the free energy of the real system and the free energy of the two bulk phases and the area of the surface between the phases.

The free energy per molecule in the nonuniform system is given by $\mu + \varphi + \psi - p/n$ and consequently

$$\gamma = \frac{1}{A}\int_V (\mu + \varphi + \psi) n dV - \frac{1}{A}\left[\int_V p dV - \mu_{01}N_{01} + p_{01}V_{01} - \mu_0 N_{02} + p_{02}V_{02}\right] \tag{31}$$

Using Equation (16) with $\mu_{01} = \mu_{02} \equiv \mu_0$ and $p_{01} = p_{02} \equiv p_0$, one obtains

$$\gamma = \int_{-\infty}^{+\infty} [p_0 - p(z)]\, dz \tag{32}$$

Equation (32) has the same form as the one given by the hydrostatic theory with the difference that $p(z)$, the local pressure which appears instead of the tangential pressure, has a clear physical meaning and may be calculated by means of the above-mentioned equations.

For obtaining γ one must solve Equation (16), which gives n and then Equation (17) which gives p; finally one integrates Equation (32).

Solid-Fluid Interface

The nonuniformity is due in this case to the external field $\psi(z)$ caused by the solid surface. In this case the equilibrium equation becomes

$$\mu[n(z)] + \psi(z) = \mu_0 \tag{33}$$

where μ_0 is the chemical potential in the bulk of the fluid phase.

The interfacial tension is given by the equation

$$\gamma = \int_{\tau}^{\infty} [p_0 - p(z)]\, dz \tag{34}$$

where τ represents the sum of the radii of the adsorbed molecule and that of the atoms from the solid wall.

The isothermal heat of wetting (or adsorption for a gas) per unit surface results from

$$q = T\int_{\tau}^{\infty} (sn - s_0 n_0)\, dz \tag{35}$$

where $s = -(\partial\mu/\partial T)_p$ and $s_0 = -(\partial\mu_0/\partial T)_p$ are the entropies per molecule.

For the number of molecules adsorbed on unit area of the solid we have

$$N = \int_{\tau}^{\infty} [n(z) - n_0]\, dz \tag{36}$$

Heterogeneous Nucleation on a Plane Solid Surface

Experiment (*20*) shows that when a freshly cleaved plane surface of mica is introduced into an undercooled vapor, a very thin liquid film appears that is able to nucleate the liquid phase only if the undercooling is sufficiently large. We notice that in the mentioned paper it is stressed that the above film is not formed by the coalescence of small drops.

The nucleation via plane films cannot be treated by means of Gibbs' theory. Gibbs' formula $\Delta T = 2\gamma v/R\Delta s$ predicts that for $R \longrightarrow \infty$ a nucleus is critical even for zero undercooling, a result in contradiction with the mentioned experiment. The work of formation of a spherical nucleus given by Gibbs' theory is infinite for $R \longrightarrow \infty$ and the work per unit surface area of the nucleus is finite and independent of the film thickness. For a plane film it is however expected that the work of formation per unit surface area should depend on the film thickness.

In what follows the nucleation via plane systems on a solid surface will be treated by means of the present approach.

Owing to the density fluctuation and to the ordering action of the solid surface, nonuniform regions appear in the undercooled system; some of these which are in a state of meta-stable equilibrium (the critical ones) are able to grow and to generate a new phase. The condition of meta-stable equilibrium leads, for the density distribution of the critical nucleus, to

$$\mu_0 = \mu + \psi + \varphi = \mu[n(z), T] + K(z)\frac{d^2n}{dz^2} + \psi(z) \tag{37}$$

The first equality is Equation (16), where $\Phi = \varphi + \psi$ takes into account via φ the effect of fluctuation and via ψ the presence of the wall. The second is a consequence of Equation (21).

The work of formation of a nucleus will be calculated for two distinct situations. In the first one, the heterogeneity exists in the vapor phase before the system is undercooled. Such a situation occurs when vapor having dust particles is condensing. In this case, the adsorption preexists the fluctuation and the formation work of the nucleus is the work W' of the formation of a fluctuation in the adsorbed system.

$$-\frac{W'}{A} = \int_{\tau}^{\infty}\left[\mu[n(z)] + \varphi + \psi - \frac{p}{n}\right] ndz - \int_{\tau}^{\infty} [\mu[n'(z)] + \psi - p'/n]\, n' dz \tag{38}$$

In the first integral the density is given by Equation (37) and the pressure is calculated from $d\mu/dp = 1/n$; in the second the density is given by Equation (33) and is calculated from $d\mu(n')/dp' = 1/n'$.

Using Equations (38) and (37) one may write

$$-\frac{W'}{A} = \int_{\tau}^{\infty} (\mu_0 - p/n)\, n dz - \int_{\tau}^{\infty} (\mu_0 - p'/n')\, n dz$$

$$= \mu_0 \int_{\tau}^{\infty} (n - n')\, dz + \int_{\tau}^{\infty} (p' - p)\, dz \qquad (39a)$$

Therefore the work of formation is composed of two terms: the first is the work needed for changing the density distribution from that of the adsorbed system to that of the critical nucleus, when the molecules originate from the undercooled bulk phase; the second term is the work needed for changing the pressure distribution. The second situation may occur when the heterogenities are introduced into an undercooled vapor. This situation occurs, for instance, in the Wilson cloud chamber; the "solid" is the ion and the potential which causes "adsorption" is its electrostatic potential.

It is possible that at the first contact between heterogeneity and vapor, fluctuation and adsorbtion occur simultaneously. The work of formation for the formation of a nucleus is then

$$-\frac{W}{A} = \int_{\tau}^{\infty} [\mu(n) + \psi + \varphi - p/n]\, n dz - \int_{\tau}^{\infty} (\mu_0 - p_0/n_0)\, n_0\, dz$$

Using Equation (37) one obtains

$$-\frac{W}{A} = \mu_0 \int_{\tau}^{\infty} (n - n_0)\, dz + \int_{\tau}^{\infty} (p_0 - p)\, dz \qquad (39b)$$

The two terms of Equation (39*b*) may be interpreted as those from Equation (39*a*).

Some significant length δ_1, δ_2 may be introduced by means of the expressions

$$\left| \int_{\tau}^{\delta_1} (n - n_0)\, dz - \int_{\tau}^{\infty} (n - n_0)\, dz \right| \leq \lambda$$

$$\left| \int_{\tau}^{\delta_2} (p - p_0)\, dz - \int_{\tau}^{\infty} (p - p_0)\, dz \right| \leq \lambda \qquad (40)$$

where λ is a small arbitrary quantity. The largest of the lengths δ_1 or δ_2 represents the extent of the nucleus.

Since the nonuniformity is decaying at not too large distances from the solid surface, the work of formation per unit area has a finit value dependent on the thickness δ of the plane nucleus.

Disjoining Pressure

A molecule at the distance z is in interaction with both plates; therefore it is under the action of the field

$$\psi(z) + \psi(h - z)$$

The equilibrium equation has the form

$$\mu(n, T) + \psi(z) + \psi(h - z) = \mu_0 \qquad (41)$$

The density and the pressure distribution may be obtained as in the cases discussed above. The thermodynamic treatment is the same as the one used in the frame of the first approach. For the disjoining pressure one obtains

$$\pi = \frac{1}{h} \int_{0}^{h} (p_0 - p)\, dz \qquad (42)$$

The pressure p may be obtained effectively by means of Equation (41) (which gives the density distribution) completed by Equation (17).

Adsorption from Multicomponent Systems

For a multicomponent system the fundamental thermodynamical equation has the form

$$\delta E = T\delta S - p\delta V + \sum_{j} (\mu_j + \varphi_j + \psi_j)$$

The condition of diffusional equilibrium leads to

$$\mu_j + \varphi_j + \psi_j = \mu_{j0} \qquad (43)$$

Since μ_j are the chemical potentials of an uniform system of density $n(z)$ and composition $x_j(z)$, one may use for them the equations

$$\frac{d\mu_k}{dz} = v_k \frac{dp}{dz} + \sum_{j=2}^{m} \frac{\partial \mu_k}{\partial x_j} \frac{dx_j}{dz} \qquad (44)$$

and also the Gibbs-Duhem equation which for $dT/dz = 0$ has the form

$$\sum_{j=1}^{m} N_j d\mu_j = V dp \qquad (45)$$

where m is the number of components.

Since from Equation (43) we have

$$\frac{d\mu_j}{dz} + \frac{d(\varphi_j + \psi_j)}{dz} = 0 \qquad (46)$$

Equation (45) leads to

$$\sum_{j=1}^{m} N_j \frac{d(\varphi_j + \psi_j)}{dz} + \frac{V dp}{dz} = 0 \qquad (47)$$

It may be noted that Equations (44) and (47) are not independent. Indeed, multiplying Equation (44) by N_k summing over k and taking into account that

$$\sum_{j=1}^{m} N_j v_j = V \quad \text{and} \quad \sum_{j=1}^{m} N_j \frac{\partial \mu_j}{\partial x_k} = 0$$

one obtains Equation (47).

Eliminating dp/dz between Equations (47) and (44) and taking Equation (46) into account, there results

$$\frac{d(\varphi_j + \psi_j)}{dz} = -\frac{v_j}{V} \sum_{j=1}^{m} N_j \frac{d(\varphi_j + \psi_j)}{dz} + \sum_{k=2}^{m} \frac{\partial \mu_j}{\partial x_k} \frac{dx_k}{dz} \qquad (48)$$

The system of Equations (47) and (46) allows one to obtain the dependence of p and of x_k on z. For a binary ideal gas mixture one obtains

$$-x_2 X_1 \frac{d\psi_1}{dz} + \frac{d\psi_2}{dz} (1 - x_2 X_2) + kT \frac{d \lg x_2}{dz} = 0 \qquad (49)$$

This differential equation solved for the boundary condition $x_2 \longrightarrow X_2$ for $z \longrightarrow \infty$ permits one to obtain x_2 as a function of z.

Chemical Reaction in the Presence of a Solid Surface

If in the presence of a solid surface a chemical reaction $\sum_j \nu_j A_j = 0$ is taking place, the equilibrium condition should be

$$\sum_{j} \nu_j (\mu_j + \psi_j) = 0 \qquad (50)$$

Since $\mu_j(z)$ is the chemical potential of an uniform system, one has

$$\mu_j = \mu_j^{\theta}(T_0, p) + kT_0 \lg(\gamma_j x_j) = \mu_j^{\theta}(T_0, p_0) + (p - p_0)\left(\frac{\partial \mu_j^{\theta}}{\partial p}\right)_{p=p_0} + kT_0 \lg \gamma_j x_j$$

Observing that $\Sigma_j \nu_j \mu_j^{\theta}(T_0, p_0) = -kT_0 \lg K_0$ where K_0 is the equilibrium constant in the bulk uniform system, we have

$$\prod_j (\gamma_j x_j)^{\nu_j} = K_0 \exp\left[-\frac{\Sigma \nu_j \psi_j}{kT_0}\right] \exp\left[-\frac{(p - p_0)}{kT_0}\sum_j \nu_j \frac{\partial \mu_j^{\theta}(T_0, p_0)}{\partial p_0}\right]$$

In the points in which z is larger than about 10 molecular thicknesses, $\psi_j = p - p_0 = 0$ and the chemical reaction takes place as in a system where the solid surface is lacking. For smaller distances, for systems which are located on the very fine pores of a solid, such as in the cracks of glass vessels or in the small spaces of the biological systems, the equilibrium may be strongly affected.

NOTATION

a = van der Waals constant, Equation (26)
A = area of the plane nonuniform system
A_j = chemical reactant
$\mathcal{A}$ = surface which envelops the volume V
b = van der Waals constant, Equation (26)
d = thickness of the nonuniform system
E = energy
E_{tot} = energy of the system between plates plus the energy of the bulk
E_{ex} = excess energy of the nonuniform system with respect to a uniform one
f = free energy per cubic centimeter of the nonuniform system
$f_0[n(z)]$ = free energy per cubic centimeter of a uniform system having the density $n(z)$
F = total free energy of a nonuniform system
$g(\vec{r}_1, \vec{r}_2)$ = radial distribution function
h = distance between the parallel plates
h^* = see Figure 2a
k = Boltzman constant
$K(z)$ = quantity as defined by Equation (21)
k_1, k_2 = functions of density not dependent on density gradients
K_0 = equilibrium constant in a bulk phase
m = number of components
$n(z)$ = density (molecules/cc.) in point z
N = total number of molecules
$\mathcal{N}$ = quantity as defined by Equation (8)
$\overline{p}$ = quantity as defined by Equation (7)
p = pressure
p_0^v = vapor pressure of a liquid bulk phase
p_t = "tangential pressure" in hydrostatical model
R = radius of the critical nucleus
r_{12} = distance between molecules 1 and 2
$\vec{r}_1$ = position vector of the molecule 1
r_0 = van der Waals radius of a molecule, Equations (22*a*) and (22*b*)
Δs = molecular entropy of vaporization
s = entropy per molecule
S = total entropy
T = temperature, °K.
ΔT = undercooling, °K.
$u(r_{12})$ = interaction energy between two molecules
v = volume per molecule
V = total volume
$\mathcal{V}$ = Ah, Equation (7)
W = work of formation of a nucleus from uniform undercooled vapor in the neighborhood of a solid surface
W' = work of formation of a nucleus from adsorbed undercooled vapor
$x_j(z)$ = molar fraction of component j in point z
$X_j = N_j/N$ = global molar fraction
z = coordinate, normal to the planes of equal density
z_i = coordinate z for the molecules from cell i

Greek Letters

$\alpha = 2a/bkT$
γ = excess free energy per unit surface
γ_j = activity coefficient for substance A_j
δ_1, δ_2 = lengths as defined by Equations (40)
ε_i = free energy of unit surface area of the wall located between cells i and $i + 1$
ε = energy constant in the interaction energy of two molecules
η = quantity as defined by Equation (10)
$\theta = bn(z)$
$\mu[n(z), T]$ = chemical potential of a uniform system with density $n(z)$
μ^{θ} = standard chemical potential
$\overline{\mu}$ = defined by Equation (8)
μ_0^v = chemical potential of the saturated vapor bulk phase
ν_j = number of molecules of substance A_j formed in reaction
Π = disjoining pressure
τ = sum of radius of a molecule from the liquid phase and the radius of a molecule from the solid wall
φ = energy per molecule in the external field caused by the nonuniformity of the system
$\Phi = \varphi + \psi$
ψ = energy of a molecule, due to the presence of a solid surface

Subscripts

i = cells
j, k = substances
$0, 01; 02$ = bulk phases

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