

Free Energy of a Nonuniform System. I. Interfacial Free Energy

JOHN W. CAHN AND JOHN E. HILLIARD
General Electric Research Laboratory, Schenectady, New York
 (Received July 29, 1957)

It is shown that the free energy of a volume V of an isotropic system of nonuniform composition or density is given by: $N_V \int_V [f_0(c) + \kappa(\nabla c)^2] dV$, where N_V is the number of molecules per unit volume, ∇c the composition or density gradient, f_0 the free energy per molecule of a homogeneous system, and κ a parameter which, in general, may be dependent on c and temperature, but for a regular solution is a constant which can be evaluated. This expression is used to determine the properties of a flat interface between two coexisting phases. In particular, we find that the thickness of the interface increases with increasing temperature and becomes infinite at the critical temperature T_c , and that at a temperature T just below T_c the interfacial free energy σ is proportional to $(T_c - T)^{1/2}$.

The predicted interfacial free energy and its temperature dependence are found to be in agreement with existing experimental data. The possibility of using optical measurements of the interface thickness to provide an additional check of our treatment is briefly discussed.

1. INTRODUCTION

IN most previous theoretical treatments of interfacial energies the interface has been arbitrarily restricted to some predetermined thickness. Thus Young^{1(a)} and Becker^{1(b)} assumed that two adjoining phases are homogeneous up to their common interface, while others^{2(a),(b)} have made calculations based on the existence of a single intermediate layer. Though such assumptions may be justifiable in certain instances,³ it is evident that they are incorrect in principle since, once the temperature and pressure of the system are specified, the interfacial thickness is no longer an independent variable.

Many years ago, Rayleigh⁴ noted that the expression derived by Young^{1(a)} was of such a form that the tension of an interface should be inversely proportional to the number of intermediate layers plus one. However, Rayleigh neglected to take into account the increase in free energy resulting from the introduction of non-equilibrium material in a diffuse interface, and he was therefore unable to estimate the interfacial thickness. The first calculation of the equilibrium thickness was apparently made by Ono⁵ (and later repeated, independently, by Hillert⁶). Though the approach used by these two authors is undoubtedly correct, it requires the numerical solution of a set of difference equations for each particular case. This procedure is not only tedious, but also obscures certain properties of the interfacial energy and precludes its expression in an analytical form. In addition, the calculations were based on the

nearest neighbor regular solution* model and there is thus some doubt as to their general validity.

The treatment that we will adopt is analogous in some respects to those used for the evaluation of the energy of magnetic⁷ and ferroelectric⁸ domain walls, and of the interface between a metal in its normal and superconducting states.⁹ We will derive a general equation for the free energy of a system having a spatial variation in one of its intensive scalar properties, such as composition or density. We will refer to such a system as being "nonuniform." In a subsequent paper we will use this equation as the starting point for a new theory of three-dimensional nucleation. For the present, however, we will confine its application to determining the free energy of a flat interface between two coexisting phases. This will include both a general treatment (Sec. 2) and an evaluation (Sec. 3) in terms of the regular solution theory. In Sec. 4 we will check the predicted interfacial free energy against existing experimental data. The paper will conclude with a brief discussion of certain optical methods which might provide an additional experimental check on the validity of our treatment.

2. GENERAL TREATMENT

a. Free Energy of a Nonuniform System

The following analysis is valid for any intensive scalar property of the system other than temperature or pressure, but to simplify the exposition we will suppose that the system is a binary solution and that the non-uniform property is c , the mole fraction of the B component. We would expect that the local free energy per molecule, $\dagger f$, in a region of nonuniform composition will depend both on the local composition and on the

¹ (a) *Miscellaneous Works of the Late Thomas Young*, George Peacock, editor (J. Murray, London, 1855), Vol. 1, pp. 462-466; (b) R. Becker, *Ann. Physik* **32**, 128 (1938).

² (a) E. A. Guggenheim, *Trans. Faraday Soc.* **41**, 150 (1945); (b) R. Defay and I. Prigogine, *Bull. soc. chim. Belges* **59**, 255 (1950).

³ Murakima, Ono, Tamura, and Kurata, *Phys. Soc. Japan* **6**, 309 (1951).

⁴ Lord Rayleigh, *Phil. Mag.* **16**, 309 (1883); *ibid.* **33**, 209 (1892).

⁵ S. Ono, *Mem. Fac. Eng. Kyushu Univ.* **10**, 195 (1947).

⁶ M. Hillert, "A theory of nucleation for solid metallic solutions," D.Sc. thesis, Massachusetts Institute of Technology, Cambridge (1956).

* Several different meanings are associated with the term "regular solution." We will use it to denote a solution having an ideal configurational entropy and an enthalpy of mixing which varies parabolically with composition [see Eq. (3.1)].

⁷ F. Bloch, *Z. Physik* **74**, 295 (1932).

⁸ T. Mitsui and J. Furuchi, *Phys. Rev.* **90**, 193 (1953).

⁹ J. Bardeen, *Phys. Rev.* **94**, 554 (1954).

[†] Symbols are listed in the appendix.

composition of the immediate environment. We will therefore attempt to express f as the sum of two contributions which are functions of the local composition and the local composition derivatives, respectively.

We will assume that the composition gradient is small compared with the reciprocal of the intermolecular distance and will take c and its derivatives as independent variables. Providing f is a continuous function of these variables, it can be expanded in a Taylor series about f_0 the free energy per molecule of a solution of uniform composition c . Employing the subscripts i, j , in the usual manner to denote the successive substitution of the x, y , and z components for the variable x_i , and the subscript zero to indicate the value of the parameter in a solution of uniform composition, leading terms in the expansion for f are:

$$f(c, \nabla c, \nabla^2 c, \dots) = f_0(c) + \sum_i L_i (\partial c / \partial x_i) + \sum_{ij} \kappa_{ij}^{(1)} (\partial^2 c / \partial x_i \partial x_j) + (1/2) \sum_{ij} \kappa_{ij}^{(2)} [(\partial c / \partial x_i)(\partial c / \partial x_j)] + \dots, \quad (2.1)$$

where

$$\begin{aligned} L_i &= [\partial f / \partial (\partial c / \partial x_i)]_0, \\ \kappa_{ij}^{(1)} &= [\partial f / \partial (\partial^2 c / \partial x_i \partial x_j)]_0, \\ \kappa_{ij}^{(2)} &= [\partial^2 f / \partial (\partial c / \partial x_i) \partial (\partial c / \partial x_j)]_0. \end{aligned} \quad (2.2)$$

In general, $\kappa_{ij}^{(1)}$ and $\kappa_{ij}^{(2)}$ are tensors reflecting the crystal symmetry and the L_i 's are components of a polarization vector in a polar crystal. For a cubic crystal or an isotropic medium (and these are the only cases that we will consider) the free energy must be invariant to the symmetry operations of reflection ($x_i \rightarrow -x_i$) and of rotation about a fourfold axis ($x_i \rightarrow x_j$). Therefore,

$$\begin{aligned} L_i &= 0, \\ \kappa_{ij}^{(1)} &= \kappa_1 = [\partial f / \partial \nabla^2 c]_0 \quad \text{for } i = j, \\ \kappa_{ij}^{(1)} &= 0 \quad \text{for } i \neq j, \\ \kappa_{ij}^{(2)} &= \kappa_2 = [\partial^2 f / \partial (\partial |\nabla c|)^2]_0 \quad \text{for } i = j, \end{aligned}$$

and

$$\kappa_{ij}^{(2)} = 0 \quad \text{for } i \neq j.$$

Hence for a cubic lattice, Eq. (2.1) reduces to†

$$f(c, \nabla c, \nabla^2 c, \dots) = f_0(c) + \kappa_1 \nabla^2 c + \kappa_2 (\nabla c)^2 + \dots \quad (2.3)$$

Integrating over a volume V of the solution we obtain for the total free energy F of this volume:

$$\begin{aligned} F &= N_V \int_V f dV \\ &= N_V \int_V [f_0(c) + \kappa_1 \nabla^2 c + \kappa_2 (\nabla c)^2 + \dots] dV, \end{aligned} \quad (2.4)$$

† This equation can also be derived as follows. If we assume that the local free energy f is a function only of f_0 and the composition derivatives then, since f , a scalar, must be invariant with respect to the direction of the gradient, only terms in even powers of the operator ∇ can appear. The leading terms of the function must therefore be of the form given in Eq. (2.3).

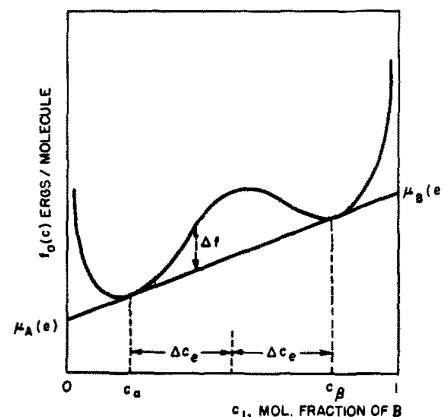


FIG. 1. $f_0(c)$ for $T < T_c$.

where N_V is the number of molecules per unit volume. By applying the divergence theorem we obtain:

$$\begin{aligned} \int_V (\kappa_1 \nabla^2 c) dV &= - \int_V (d\kappa_1 / dc) (\nabla c)^2 dV \\ &\quad + \int_S (\kappa_1 \nabla c \cdot n) dS. \end{aligned} \quad (2.5)$$

Since we are not concerned with effects at the external surface, we can choose a boundary of integration in Eq. (2.4) in such a manner that $\nabla c \cdot n$ is zero at the boundary. The surface integral therefore vanishes and we can employ Eq. (2.5) to eliminate the term in $\nabla^2 c$ from Eq. (2.4) to obtain:

$$F = N_V \int_V [f_0 + \kappa (\nabla c)^2 + \dots] dV, \quad (2.6)$$

where

$$\begin{aligned} \kappa &= -d\kappa_1 / dc + \kappa_2 \\ &= -[\partial^2 f / \partial c \partial \nabla^2 c]_0 + [\partial^2 f / \partial (\partial |\nabla c|)^2]_0. \end{aligned} \quad (2.7)$$

Equation (2.6) is the central one of the treatment. It reveals that, to a first approximation, the free energy of a small volume of nonuniform solution can be expressed as the sum of two contributions, one being the free energy that this volume would have in a homogeneous solution and the other a "gradient energy" which is a function of the local composition.

b. Free Energy of a Flat Interface

We will consider a flat interface of area A between two coexisting isotropic phases α and β of composition§ c_α and c_β . It will be assumed that the free energy of non-equilibrium material of composition intermediate between c_α and c_β can be represented by a continuous function $f_0(c)$ of the form shown in Fig. 1.

§ If ρ_L and ρ_V (the densities, respectively, of a pure liquid and its vapor) are substituted for c_α and c_β , then the equations derived in this section will apply specifically to an interface between the condensed phase and its vapor.

Applying Eq. (2.6) to the one-dimensional composition change across the interface, and neglecting terms in derivatives higher than the second, we obtain for the total free energy F of the system:

$$F = AN_V \int_{-\infty}^{+\infty} [f_0(c) + \kappa(dc/dx)^2] dx. \quad (2.8)$$

The specific interfacial free energy, σ , is by definition the difference per unit area of interface between the actual free energy of the system and that which it would have if the properties of the phases were continuous throughout. Hence:

$$\sigma = N_V \int_{-\infty}^{+\infty} [f_0(c) + \kappa(dc/dx)^2 - c\mu_B(e) - (1-c)\mu_A(e)] dx, \quad (2.9)$$

where $\mu_A(e)$ and $\mu_B(e)$ are the chemical potentials per molecule (referred to the same standard states as f_0) of the species A and B in the α or β phase. For σ to be uniquely defined it is obviously necessary that the chemical potential of a particular species be the same in both phases and therefore that the two phases be in equilibrium—a condition which is not required for calculating the energy of an interface with an abrupt composition change. Equation (2.9) can be rewritten:

$$\sigma = N_V \int_{-\infty}^{+\infty} [\Delta f(c) + \kappa(dc/dx)^2] dx, \quad (2.10)$$

where $\Delta f(c)$ is defined by

$$\Delta f(c) = f_0(c) - [c\mu_B(e) + (1-c)\mu_A(e)] \quad (2.11)$$

$$= c[\mu_B(c) - \mu_B(e)] + (1-c)[\mu_A(c) - \mu_A(e)]. \quad (2.12)$$

$\Delta f(c)$ may therefore be regarded as the free energy referred to a standard state of an equilibrium mixture of α and β [Eq. (2.11)], or as the free energy per molecule of transferring material from an infinite reservoir of composition c_α or c_β to material of composition c [Eq. (2.12)].

According to Eq. (2.10) the more diffuse the interface is, the smaller will be the contribution of the gradient energy term, $\kappa(dc/dx)^2$, to σ . But this decrease in energy can only be achieved by introducing more material at the interface of nonequilibrium composition and thus at the expense of increasing the integrated value of $\Delta f(c)$. At equilibrium the composition variation will be such that the integral in Eq. (2.10) is a minimum. (This is equivalent to the requirement that the chemical potentials be constant throughout the system.)

If we substitute the integrand of Eq. (2.10) in the Euler equation, we will obtain a differential equation whose solutions are the composition profile corresponding to stationary values (i.e., maxima, minima, or saddle points) of the integral. Since the integrand does

not explicitly depend on x , the appropriate form¹⁰ of the Euler equation is

$$I - (dc/dx)[\partial I / \partial (dc/dx)] = 0,$$

where I represents the integrand. We thus obtain as the condition for a stationary value:

$$\Delta f(c) - \kappa(dc/dx)^2 = \text{const.} \quad (2.13)$$

The constant in this equation must be zero since $\Delta f(c)$ and (dc/dx) both tend to zero as $x \rightarrow \pm \infty$. Hence for a minimum value of σ :

$$\Delta f(c) = \kappa(dc/dx)^2. \quad (2.14)$$

Using this expression to eliminate $\kappa(dc/dx)^2$ from Eq. (2.10) we find:

$$\sigma = 2N_V \int_{-\infty}^{+\infty} \Delta f(c) dx.$$

Changing the variable of integration from x to c by means of Eq. (2.14), we finally obtain^{||}:

$$\sigma = 2N_V \int_{c_\alpha}^{c_\beta} [\kappa \Delta f(c)]^{1/2} dc. \quad (2.15)$$

In the next section we will use the regular solution theory for a numerical evaluation of σ . The general treatment can, however, be taken a step further to determine the functional dependence of σ on temperature in the immediate vicinity of the critical (or conjugate) temperature T_c at which the two phases attain the same critical composition c_c .

If f_0 can be expanded in a Taylor series about T_c and

¹⁰ H. Margenau and G. M. Murphy, *The Mathematics of Physics and Chemistry* (D. Van Nostrand Company, Inc., Princeton, 1943), p. 195.

^{||} An interface between two fluids which differ in more than one scalar parameter is considerably more complicated. Consider the case in which two parameters, n and m , determine the free energy $\Delta f(n, m)$ and let the corresponding gradient energy coefficients be κ_n and κ_m . The interfacial energy is the minimum of:

$$N_V \int_{-\infty}^{+\infty} [\Delta f(n, m) + \kappa_n (dn/dx)^2 + \kappa_m (dm/dx)^2] dx$$

where we have neglected the cross term. The Euler equations for this problem yield:

$$\partial \Delta f / \partial n = \kappa_n (d^2 n / dx^2)$$

and

$$\partial \Delta f / \partial m = \kappa_m (d^2 m / dx^2).$$

These can be combined to give:

$$\sigma = 2N_V \int_{c_\alpha}^{c_\beta} (\kappa_n \Delta f)^{1/2} [1 + (\kappa_m / \kappa_n) (dm/dn)^2]^{1/2} dn,$$

which reduces to Eq. (2.15) if m is a constant or κ_m is small. The way m changes with n through the interface is found by solving the two Euler equations to eliminate x . The solution will correspond to the trajectory of a particle of unit mass having a vanishing total energy (kinetic and potential) on a potential surface given by: $-\Delta f(n, \sqrt{\kappa_n / \kappa_m} m)$. The particle starts from one of the coexisting phases and slides to the other; it does not follow potential troughs but banks on curves to reduce gradient energy at the expense of volume energy. There may be several different paths, all of which represent stationary values of the interfacial free energy, but only the path having the lowest free energy will correspond to the actual interface.

c_e , the following expression can be derived for Δf :

$$\Delta f_{(T \sim T_c)} = -\beta(T_c - T)[(\Delta c)^2 - (\Delta c_e)^2] + \gamma[(\Delta c)^4 - (\Delta c_e)^4] + \dots \quad (2.16)$$

in which $\Delta c = (c - c_e)$, $\Delta c_e = (c_\beta - c_e) = (c_e - c_\alpha)$ and β and γ are inherently positive constants defined by the following derivatives of f_0 evaluated at $c = c_e$ and $T = T_c$:

$$\beta = (\partial^3 f_0 / \partial T \partial c^2) / 2! \quad (2.17)$$

$$\gamma = (\partial^4 f_0 / \partial c^4) / 4! \quad (2.18)$$

This expansion gives the following relationships:

$$(\Delta c_e)^2_{(T \sim T_c)} = \beta(T_c - T) / 2\gamma, \quad (2.19)$$

$$(\Delta f)_{(T \sim T_c)} = \gamma[(\Delta c_e)^2 - (\Delta c)^2]^2. \quad (2.20)$$

From Eqs. (2.15) and (2.20) we obtain:

$$(\sigma)_{(T \sim T_c)} = 2N_V \int_{-\Delta c_e}^{+\Delta c_e} (\kappa \gamma)^{1/2} [(\Delta c_e)^2 - (\Delta c)^2] d(\Delta c). \quad (2.21)$$

If in the vicinity of the critical point, κ is continuous and nonvanishing, then we may, sufficiently close to T_c , neglect any variations in κ and assume it constant. This is equivalent to expanding κ about the critical point and neglecting higher terms, or to applying the mean value theorem. Thus, we can evaluate the integral of Eq. (2.21) and use (2.19) to obtain:

$$(\sigma)_{(T \sim T_c)} = (2\sqrt{2}N_V/3\gamma)\kappa^{1/2}\beta^{1/2}(T_c - T)^{3/2}. \quad (2.22)$$

Our analysis, therefore, predicts that near the critical temperature the interfacial free energy should be proportional to $(T_c - T)^{3/2}$. It is fairly easy to prove that any model which confines the thickness of the interface to a fixed number (say p) of molecular planes leads to an expression for σ which is proportional to $(T_c - T)/(p+1)$ and is thus linearly dependent on temperature.[¶]

According to Eq. (2.19) the coexistence curve should be parabolic in the immediate vicinity of c_e . It can be shown¹¹ that this functionality should also apply to the density of a liquid and its saturated vapor near the critical point. This is found to be true for certain

[¶] This may be proved as follows: let the composition difference between the i th plane and its neighbor be $y_i \Delta c_e$. The energy of the interface between these two planes is therefore proportional to $(y_i \Delta c_e)^2$. The total interfacial energy will be proportional to the

sum $(\Delta c_e)^2 \sum_{i=0}^p (y_i)^2$, plus the sum, $\sum_{i=0}^p \Delta f_i$, of the volume free energy terms. Sufficiently close to the critical point the latter contribution can be neglected since it varies as $(T_c - T)^2$ whereas $(\Delta c_e)^2$ varies as $(T_c - T)$. The minimum of $(\Delta c_e)^2 \sum_{i=0}^p (y_i)^2$ subject to the condition

$\sum_{i=0}^p y_i = 1$ occurs when each $y_i = 1/(p+1)$. Hence $(\sigma)_{T \sim T_c} \propto (T_c - T)/(p+1)$. It is interesting to note that this is the expression derived by Rayleigh.⁴

¹¹ R. Fowler and E. A. Guggenheim, *Statistical Mechanics* (Cambridge University Press, London, 1949), pp. 316-318.

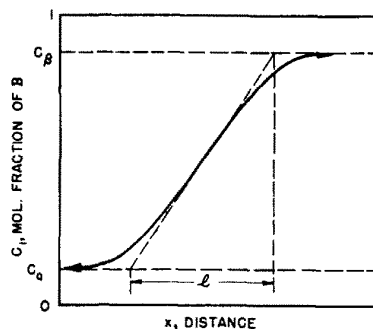


FIG. 2. Interface profile.

systems^{12,13} but the coexistence curves for many gases¹⁴ and binary liquid mixtures^{15,16} appear to be cubic; i.e., $(T_c - T)$ in such cases is approximately proportional to $(|\Delta c_e|)^3$. So far there appears to be no satisfactory explanation for this anomaly. Since we have used Eq. (2.19) in deriving Eq. (2.22) the latter is strictly valid only for those systems having a parabolic coexistence curve. However, we will later show that it may also be a good approximation for the other systems.

c. Composition Profile and Thickness of Interface

The composition variation across the interface as determined by Eq. (2.14) is such that:

$$dc/dx = (\Delta f/\kappa)^{1/2}. \quad (2.23)$$

Inspection of the Δf function (Fig. 1) indicates that to satisfy Eq. (2.23) the composition profile must be sigmoid in shape as shown in Fig. 2.

In the vicinity of the critical point we can make the appropriate substitutions from Eqs. (2.19) and (2.20) and integrate Eq. (2.23) (assuming as before that κ is constant) to obtain

$$(\Delta c/\Delta c_e)_{(T \sim T_c)} = \tanh\{[\beta(T - T_c)/2\kappa]^{1/2}x\}, \quad (2.24)$$

where the distance x is measured from an origin at $\Delta c = 0$ (i.e., $c = c_e$). Using this equation, the thickness l of the interface could be defined as the distance x for a given $\Delta c/\Delta c_e$ ratio. But for convenience in subsequent calculation we will express l in terms of the gradient at c_e as follows:

$$l = (c_\alpha - c_\beta) / (dc/dx)_{c_e} = 2\Delta c_e(\kappa/\Delta f_{\max})^{1/2}. \quad (2.25)$$

Near the critical temperature we obtain on substitution from Eqs. (2.23), (2.19), and (2.20):

$$l_{(T \sim T_c)} = 2[\beta/\gamma(T_c - T)]^{1/2}. \quad (2.26)$$

¹² A. Münster and K. Sagel, *Z. physik Chem.* **7**, 297 (1956).

¹³ Krichevskii, Khazanov, and Linshitz, *Doklady Akad. Nauk S.S.S.R.* **100**, 737 (1955).

¹⁴ E. A. Guggenheim, *J. Chem. Phys.* **13**, 253 (1945).

¹⁵ J. D. Cox and E. F. G. Herington, *Trans. Faraday Soc.* **52**, 926 (1956).

¹⁶ O. K. Rice, *J. Chem. Phys.* **23**, 164 (1955).

Thus we see that the thickness of the interface increases with increasing temperature and becomes infinite at the critical temperature.

Before leaving the general treatment it should be emphasized that we have tacitly assumed that κ is everywhere positive and nonvanishing. This is evidently true for the single phase region of the system as otherwise, contrary to experience, the homogeneous phase would be unstable with respect to periodic composition fluctuations. We can see no reason why κ should change sign or vanish in the unstable region, but we are unable to prove that it could not happen. If for some system there were a range over which $\kappa \leq 0$, then there would be a corresponding discontinuity in the interface profile and the treatment would have to be modified accordingly.

3. APPLICATION OF THE REGULAR SOLUTION THEORY

The determination of the absolute value of σ and its temperature dependence outside the range $T \sim T_c$ requires the use of a solution model for the evaluation of κ and the free-energy function Δf . For this purpose we believe it worthwhile to apply the regular solution theory despite its well-known shortcomings. Accordingly, we will assume that the free energy f_R of a (uniform) solution is given by:

$$f_R(c) = \omega c(1-c) + kT[c \ln c + (1-c) \ln(1-c)]. \quad (3.1)$$

The enthalpy term in this equation is usually derived¹⁷ by considering only the molecular interactions between nearest neighbors. The same result can also be obtained¹⁸ from a summation of the pairwise interactions throughout the whole system. However, as we will show, these two approaches do not lead to the same value for the gradient energy in a nonuniform solution.

a. Free Energy of a Nonuniform Regular Solution

We will first determine the enthalpy for a two-component cubic lattice. The following assumptions will be made: (1) the lattice parameter is independent of composition, (2) the intermolecular potential is a function only of the corresponding intermolecular distance, (3) the distribution of molecules on the lattice sites is locally random.

Let $C(R)$ and $C(S)$ be the probabilities of finding a B molecule at sites R and S , respectively, in the lattice. The probability, P_{AB} , that an AB bond will be formed by a B molecule at R and an A molecule at S is

$$P_{AB} = C(R)[1 - C(S)]. \quad (3.2)$$

If \mathbf{r} is the radius vector of site S relative to site R , then

¹⁷ E. A. Guggenheim, *Mixtures* (Oxford University Press, London, 1952).

¹⁸ J. H. Hildebrand and S. E. Wood, *J. Chem. Phys.* **1**, 817 (1933).

we can obtain $C(S)$ as a function of $C(R)$ by expanding about R . Thus,

$$C(S) = C(R) + (\mathbf{r} \cdot \nabla)C(R) + (1/2!)(\mathbf{r} \cdot \nabla)^2 C(R) + (1/3!)(\mathbf{r} \cdot \nabla)^3 C(R) + \dots \quad (3.3)$$

Considering now the Z_n molecules in the n th coordination shell at a radius r_n from R . The probable number of AB bonds, $Z_n(P_{AB})_n$, between a B molecule at R and the A molecules in its n th shell is, from Eqs. (3.2) and (3.3):

$$Z_n(P_{AB})_n = Z_n \{ C(R)[1 - C(R)] - C(R)[\sum (\mathbf{r} \cdot \nabla)C(R) + (1/2!)\sum (\mathbf{r} \cdot \nabla)^2 C(R)] \}, \quad (3.4)$$

where the summations are over all the sites in the n th shell, and the third and higher derivatives in Eq. (3.3) are neglected. Expressing Eq. (3.4) in terms of the vector components and performing the indicated summations** we obtain for a cubic lattice:

$$Z_n(P_{AB})_n = Z_n c(R)[1 - c(R)] - (1/6)Z_n c(R) \nabla^2 c(R),$$

where the probability C has been replaced by the corresponding mol fraction c of the B component.

If $\nu_n = E_{AB} - (1/2)(E_{AA} + E_{BB})$ where the E 's are the intermolecular potentials for the n th coordination shell then, from the previous equation, we find that the total energy per molecule at R , $u(R)$, relative to the pure components is:

$$u(R) = c(R)[1 - c(R)] \sum_n Z_n \nu_n - (1/6)c(R) \sum_n Z_n r_n^2 \nu_n. \quad (3.5)$$

As before, the energy is independent of the direction of the gradient in the lattice. Defining:

$$\omega \equiv \sum_n Z_n \nu_n \quad (3.6)$$

and

$$\lambda^2 \equiv (\sum_n Z_n r_n^2 \nu_n) / (3 \sum_n Z_n \nu_n), \quad (3.7)$$

we obtain on substitution in Eq. (3.5):

$$u(R) = \omega c(1-c) - \omega \lambda^2 c \nabla^2 c / 2. \quad (3.8)$$

For a liquid solution the coordination number Z_n is replaced by $4\pi r^2 \rho(r) dr / V$ for the probable number of molecules between r and $r + dr$, where $\rho(r)$ is the reduced radial distribution function which is assumed independent of composition and species involved. Substitution for Z_n gives for the equations corresponding to (3.6) and (3.7):

$$\omega = (4\pi/V) \int_0^\infty r^2 \rho(r) \nu(r) dr \quad (3.9)$$

** The odd and mixed derivatives cancel on summation because of the center of inversion. The remaining derivatives are summed as follows. Let the components of \mathbf{r} be h, k , and l . Providing not more than two of the components are equal, all the terms arising from permutations of h, k, l can be grouped into sets of three, thus $[(h, k, l), (k, l, h), (l, h, k)]$. Each group gives on summation $r_n^2 c(R) \nabla^2 c(R)$. When $h = k = l$, the terms can be grouped into sets of four: $[(h, h, h), (h, h, h), (h, h, h), (h, h, h)]$ giving a sum of $(4/3)r_n^2 c(R) \nabla^2 c(R)$. In either case the average contribution per molecule is $(1/3)r_n^2 c(R) \nabla^2 c(R)$.

and

$$\lambda^2 = \left[\int_0^\infty r^4 \rho(r) \nu(r) dr \right] / \left[3 \int_0^\infty r^2 \rho(r) \nu(r) dr \right]. \quad (3.10)$$

The parameter λ defined by Eqs. (3.7) and (3.10) has the dimensions of length and represents a rms effective "interaction distance" for the energy in a concentration gradient. If interactions other than those between nearest neighbors are neglected, Eq. (3.10) gives a value of $r_0/\sqrt{3}$ for λ , where r_0 is the intermolecular distance. However, if we assume that ν_n is proportional to r^{-n} and that the radial distribution function $\rho(r)$ is approximated by $\rho=1$ for $r>r_0$ and $\rho=0$ for $r<r_0$, we obtain:

$$\lambda^2 = (n-3)r_0^2/3(n-5),$$

which gives $\lambda=r_0$ for $n=6$. If a repulsive term proportional to r^{-12} is added to ν_n then λ is increased to a value of $(11/7)^{1/2}r_0$. Thus λ is very sensitive to the exact nature of the long-range interactions.

We have so far only considered the enthalpy of the solution. The entropy can be derived as follows. Assume the lattice to be composed of p equicomposition layers (not necessarily flat). Let one such layer of composition c_P contain N_P molecules. The number of ways W_P of arranging the molecules within the layer is:

$$W_P = N_P! / \{ (c_P N_P)! [(1-c_P)N_P]! \}.$$

Since the layers are of assigned composition and cannot be interchanged, the total number of ways, W , of arranging all the molecules on the lattice is merely:

$$W = \prod_P W_P.$$

Substituting for W in the Boltzmann expression:

$$S = k \ln W,$$

we obtain for the configurational entropy S ,

$$S = k \ln \left(\prod_P W_P \right) = k \sum_P \ln W_P,$$

where N is the number of molecules. Stirling's formula gives:

$$S = -k \sum_P N_P [c_P \ln c_P + (1-c_P) \ln(1-c_P)].$$

The configurational entropy per molecule $s(R)$ at lattice point R is therefore:

$$s(R) = -k [c \ln c + (1-c) \ln(1-c)], \quad (3.11)$$

which is identical to the entropy in a uniform solution of composition c ; consequently there is no contribution to the entropy from a composition gradient.

Comparing coefficients in Eqs. (3.8) and (2.3) and using the subscript "R" to denote the value of a parameter for a regular solution, we find: $\kappa_{2R}=0$ and $\kappa_{1R} = -c\omega\lambda^2/2$. Thus Eq. (2.7) gives

$$\kappa_R = \omega\lambda^2/2. \quad (3.12)$$

According to Eqs. (2.6) and (3.12) the total free energy F_R is therefore:

$$F_R = N_V \int_V [f_R + (\omega\lambda^2/2)(\nabla c)^2] dV. \quad (3.13)$$

b. Interfacial Free Energy of a Regular Solution

In addition to the preceding results we will utilize the following well known properties¹⁷ of a regular solution,

$$c_e = \frac{1}{2}, \quad (3.14)$$

$$\mu_A = \omega c^2 - kT \ln(1-c), \quad (3.15)$$

$$\omega = 2kT_e, \quad (3.16)$$

$$\ln[c_e/(1-c_e)] = (2c_e-1)\omega/kT. \quad (3.17)$$

From Eqs. (2.11) and (3.15) we obtain

$$\begin{aligned} \Delta f_R &= -\omega(c-c_e)^2 + kT \{ c \ln(c/c_e) \\ &\quad + (1-c) \ln[(1-c)/(1-c_e)] \} \\ &= f_R(c) - f_R(c_e), \end{aligned} \quad (3.18)$$

in which c_e can be set equal to either of the equilibrium compositions c_α or c_β . Differentiating Eq. (3.18) and substituting in (2.17) and (2.18) gives:

$$\beta_R = 2k,$$

$$\gamma_R = 4kT_e/3.$$

We have now evaluated all the parameters introduced into the general treatment Sec. 2.

Making the appropriate substitutions in Eq. (2.15) we obtain for σ_R :

$$\sigma_R = 2N_V \lambda k T_e \sigma_r, \quad (3.19)$$

where σ_r is a reduced interfacial energy defined by

$$\sigma_r = \int_{c_\alpha}^{c_\beta} (\Delta f_R / kT_e) \frac{1}{2} dc. \quad (3.20)$$

This integral has been evaluated numerically and is plotted in Fig. 3 as σ_r versus T/T_e and in Fig. 4 as $\log(\sigma_r)$ versus $\log(1-T/T_e)$. For the region $T \sim T_e$ Eq. (2.22) gives

$$(\sigma_R)_{(T \sim T_e)} = 2N_V \lambda k T_e [(T_e - T)/T_e]^{\frac{1}{2}}. \quad (3.21)$$

An expression can also be derived for the case $T \sim 0$. At low temperatures the entropy term in Eq. (3.18) is small compared with that for the enthalpy, and c_e is approximately equal to 1 or 0. Equation (3.20) can therefore be approximated by

$$\begin{aligned} (\sigma_R)_{(T \sim 0)} &= 2\sqrt{2} N_V \lambda k T_e \int_0^1 \{ [c(1-c)]^{\frac{1}{2}} \\ &\quad + T [c \ln c + (1-c) \ln(1-c)] / 4T_e [c(1-c)]^{\frac{1}{2}} \} dc. \end{aligned}$$

Evaluating the first term of the integral analytically and

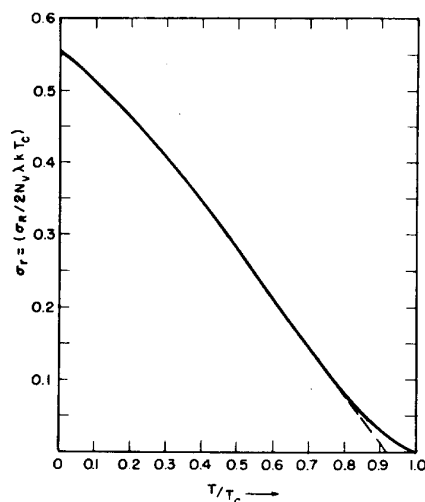


FIG. 3. Reduced interfacial free energy (σ_r) versus T/T_c for a regular solution.

the second term numerically, we obtain

$$(\sigma_R)_{(T \sim 0)} = 2N_v \lambda k T_c [(\pi/4\sqrt{2}) - 0.426(T/T_c)]. \quad (3.22)$$

An approximate expression for σ_R which is valid over the whole temperature range can be obtained by noting that:

$$\sigma_r = \phi [\Delta f_{R(\max)} / k T_c]^{1/2} \Delta c_e,$$

where, as will be seen from Eqs. (3.21) and (3.22), ϕ varies from $\frac{1}{2}$ at $T = T_c$ to $\pi/2$ at $T = 0$. Using a linear interpolation for ϕ we find:

$$\sigma_R \sim 2N_v \lambda [k T_c]^{1/2} [\pi \Delta c_e (\Delta f_{R(\max)})^{1/2} / 2] \times [1 - (\pi/2 - \frac{1}{2})(T/T_c)]. \quad (3.23)$$

This equation in conjunction with (3.17) and (3.18) provides a convenient means of calculating σ_R with an error not exceeding one percent.

c. Interface Profile for a Regular Solution

For a regular solution the interface profile is symmetrical about $c = \frac{1}{2}$. From Eq. (2.25) defining the thickness l , we obtain on substitution from Eqs. (2.23), (3.12), (3.17), and (3.18):

$$l_R/\lambda = \sqrt{2} \{ -1 - [T \ln 4c_e(1-c_e)] / [T_c(1-2c_e)^2] \}^{-1/2} \quad (3.24)$$

and corresponding to Eq. (2.26) we have for $T \sim T_c$:

$$(l_R/\lambda)_{(T \sim T_c)} = 2[T_c/(T_c - T)]^{1/2}. \quad (3.25)$$

The quantity l_R/λ has been calculated numerically from Eq. (3.24) and is plotted versus T/T_c in Fig. 5. It will be recalled that one of the basic assumptions we made when neglecting the higher terms in the expansion for f [Eq. (2.1)] was that the gradient was small compared with the reciprocal of the intermolecular distance. This assumption is undoubtedly valid in the critical region.

At low temperatures where there may be a steep gradient in concentration at the interface, a large error might be expected in the calculated value of σ . However this is not so, because it may be shown that our treatment is equivalent to a sharp interface in which the number of atoms per unit area of interface is $2N_v \lambda^2/3l$ which at low temperatures is approximately $3N_v \lambda/2$ and is therefore in good agreement with the number calculated for a sharp interface.

4. COMPARISON WITH EXPERIMENTAL RESULTS

If, as an approximation, one accepts the simple "hole" theory which treats a liquid as a regular solution of holes and molecules, then the equations derived in the previous section are directly applicable to the surface free energy of a pure liquid in equilibrium with its vapor. Our comparison with experimental measurements will therefore include both surface and interfacial free energies.

a. Empirical Expressions for the Surface Free Energy

It is well known that many of the experimental data for the temperature dependence of the surface energy can be fitted by certain empirical expressions. One of the earliest of these was proposed by van der Waals¹⁹ and can be written in the form:

$$\sigma = \sigma_0(1 - T/T_c)^n. \quad (4.1)$$

Ferguson^{20,21} tested this equation for a variety of organic

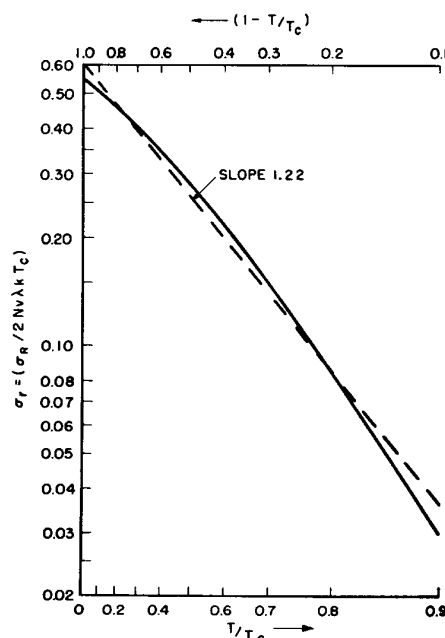


FIG. 4. $\text{Log}(\sigma_r)$ versus $\text{log}(1 - T/T_c)$ for a regular solution.

¹⁹ J. D. van der Waals, Z. physik. Chem. 13, 716 (1894).

²⁰ A. Ferguson, Trans. Faraday Soc. 19, 407 (1923).

²¹ A. Ferguson, Proc. Phys. Soc. (London) 52, 759 (1940).

liquids and found it to be satisfactory with $n=1.21$. According to Guggenheim¹⁴ a similar value (actually 11/9) for n fitted the data for liquid Ne, A, N₂, and O₂ over the limited temperature range (at most 20°C) of the measurements which were in the region of $0.6 T/T_c$. It is evident from Fig. 4 that Eq. (4.1) with $n=1.22$ would fit our predicted temperature dependence with an error of not more than a few percent over the major portion of the temperature range.

At higher temperatures, say from 0.7 to $0.9 T/T_c$, it will be seen from Fig. 3 that σ could be approximately fitted by a relationship linear in T and which extrapolates to a zero σ at a temperature δ below T_c . Thus we can write

$$\sigma = \sigma_0 [1 - (T + \delta)/T_c],$$

which will be recognized as a general form of the Ramsay-Shields equation.²²

Thus the temperature dependence of σ predicted by our treatment is consistent with that given by two relationships which, in turn, are known to be consistent with experimental measurements.

b. Absolute Surface Free Energies for Liquid Ne, A, N₂, and O₂

Equation (3.19) can be rewritten in terms of r_0 (the intermolecular distance) V_m (molar volume) and N_0 (Avogadro's number) to give:

$$\sigma_R = (2kT_c \lambda / r_0) (6/\pi)^{1/2} (N_0 V_m)^{1/2} \sigma_r,$$

and substituting for the physical constants (cgs units) we obtain:

$$\sigma_R = 2.44 (\lambda / r_0) T_c \sigma_r / V_m^{1/2} \text{ ergs cm}^{-2}. \quad (4.2)$$

If σ_R is a surface energy, the value required for V_m is the molar volume of the liquid at absolute zero. Assuming that this is $V_c/3.5$ ¹⁴ and that $\lambda/r_0 = (11/7)^{1/2}$ as evaluated in Sec. 3a for a 6-12 potential, the surface energies of liquid neon, argon, nitrogen, and oxygen have been calculated from data compiled by Guggenheim.¹⁴ The results are shown in column 7 of Table I. It will be noted that they are in good agreement with the measured values (column 6), the greatest deviation being 13.7% for neon.

TABLE I. Observed and calculated surface free energies for Ne, A, N₂, and O₂.^a

Liquid	V_c cm ³ mole ⁻¹	T_c °K	T °K	σ_r (Fig. 4)	σ_{obs} ergs cm ⁻²	σ_{calc} ergs cm ⁻² Eq. (4.2)	Diff. %
Neon	41.7	44.8	26.6	0.216	4.99	5.68	+13.7
Argon	75.3	150.7	87.0	0.226	12.68	13.45	+6.1
Nitrogen	90.2	126.0	80.0	0.188	8.27	8.32	+0.6
Oxygen	74.5	154.3	80.0	0.267	15.73	16.33	+3.8

^a Values of V_c , T_c , and σ_{obs} taken from data compiled by Guggenheim.¹⁴

²² W. Ramsay and J. Shields, Phil. Trans. A184, 647 (1893).

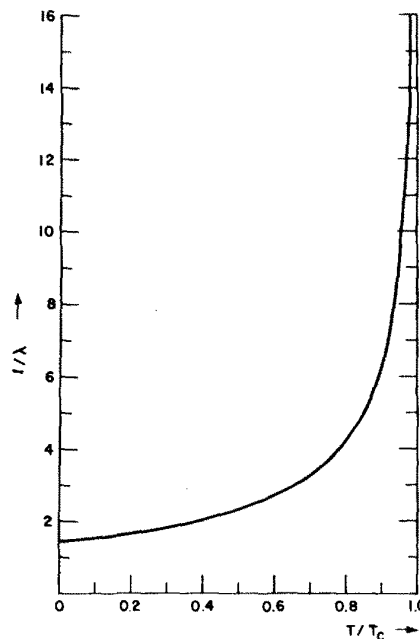


FIG. 5. l/λ versus T/T_c for a regular solution.

c. Temperature Dependence of σ in Vicinity of T_c

Apparently, the only comprehensive data available in the vicinity of the critical temperature are those of Attack and Rice²³ for the cyclohexane-aniline system. These authors determined the interfacial energy over the range of 0.35° to 3.16°C below T_c (29.582°C)¹⁶ by measurement of the capillary rise. Their results are plotted in Fig. 6 in the form of $(\sigma)^{1/2}$ versus temperature. The radii of the circles enclosing the points corresponds to an error of approximately 0.005 mm in the capillary rise. The experimental points appear to be adequately fitted by a straight line in accordance with Eq. (3.21) despite the fact that this system is one which apparently has a cubic coexistence curve in the vicinity of T_c .

Corresponding to Eq. (4.2) we have for Eq. (3.21):

$$(\sigma_R)(T - T_c) = 2.44 (\lambda / r_0) (T_c)^{-1/2} (V_m)^{-1/2} (T_c - T)^{1/2}. \quad (4.3)$$

Substituting $\lambda/r_0 = (11/7)^{1/2}$, $T_c = 302.6^\circ\text{K}$, $V_m = 102.2 \text{ cm}^3 \text{ mole}^{-1}$ (calculated using a density of 0.864 g cm^{-3} and a molecular weight of 88.1), gives a theoretical slope of $4.02 \times 10^{-2} \text{ erg}^{1/2} T^{-1} \text{ cm}^{1/2}$, which is lower than the observed slope of 7.88×10^{-2} . This deviation is not surprising since the simple model we used for calculating λ/r_0 is a poor approximation for cyclohexane-aniline solutions. The experimental data could be fitted exactly by setting $\lambda/r_0 = 3.4$. This value is not unreasonable and, furthermore, it can be independently checked by the optical method described in the next section.

²³ D. Attack and O. K. Rice, Discussions Faraday Soc. 15, 210 (1953).

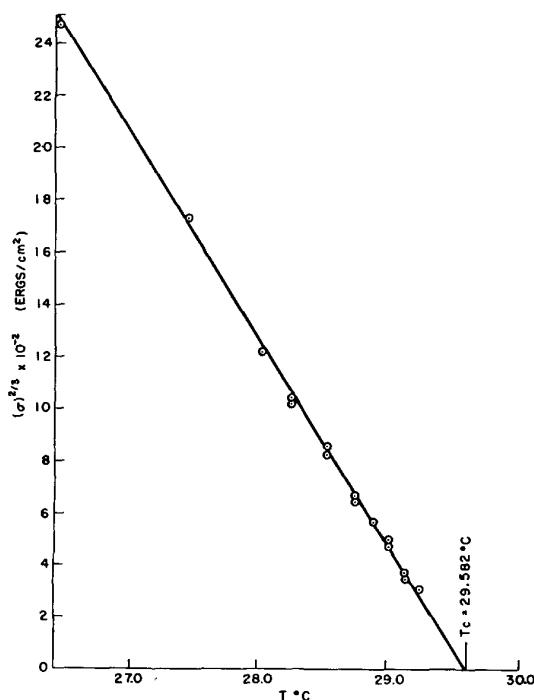


FIG. 6. Plot of $(\sigma)^{2/3}$ versus T from measurements of D. Attack and O. K. Rice²³ for the interfacial free energy (σ) between coexisting phases of cyclohexane and aniline.

5. SUGGESTED OPTICAL MEASUREMENTS

We have predicted that an interface is diffuse and that in the critical region its thickness is strongly temperature dependent. A direct measurement of the thickness would obviously be of value in providing an independent check on the values of κ or λ calculated from experimentally determined interfacial free energies.

In classical optics it is usually assumed that a reflecting interface is sharp: i.e., that there is a discontinuous change in the refractive index. In general, this assumption is satisfactory since most optical properties depend only on the difference in the refractive indices of the adjoining media. However, Drude²⁴ has shown that an exception occurs for the reflection of light which is incident at the Brewsterian angle and is polarized at 45° to the plane of incidence. Under these conditions the reflected beam is elliptically polarized with a coefficient of ellipticity $\bar{\rho}$ which depends on the diffuseness of the interface as indicated by the following equation:

$$\bar{\rho} = [\pi(\epsilon_\alpha + \epsilon_\beta)^{1/2}][\lambda_0(\epsilon_\alpha - \epsilon_\beta)]^{-1} \times \int_{-\infty}^{+\infty} [(\epsilon - \epsilon_\alpha)(\epsilon - \epsilon_\beta)/\epsilon] dx, \quad (5.1)$$

where λ_0 is the wavelength of the incident radiation, x the distance and ϵ the dielectric constant (the subscripts

²⁴ M. Born, *Optik* (Verlag Julius Springer, Berlin, 1933), p. 39, Eq. (19).

referring to the bulk liquids). Since the dependence of ϵ on distance is normally not known, this equation is usually employed in an approximate form to find the thickness of a thin intermediate layer which is assumed to have a constant value of ϵ given by the geometric mean of ϵ_α and ϵ_β . In our case this assumption is unnecessary because we have an expression for the variation of composition with x . If we assume that ϵ varies linearly with composition, we obtain upon integration of Eq. (5.1) that, in the region of the critical point,

$$\bar{\rho} = [8\pi(d\epsilon/dc)\kappa^{1/2}][\lambda_0\epsilon_c\gamma^{1/2}]^{-1}, \quad (5.2)$$

where ϵ_c is the value of ϵ at the critical composition. We thus predict that in the vicinity of the critical point the coefficient of ellipticity is temperature independent. This is because the decrease in the difference of the compositions of the two solutions is exactly compensated by the increase in the thickness at the interface. So far as we know, $\bar{\rho}$ is the only property which exhibits this behavior in the critical region and it should therefore be a particularly favorable one for experimental study.

6. SUMMARY AND DISCUSSION

In this paper and in one which is to appear subsequently, we have attempted to treat the free energies of an interface and of a critical nucleus as being particular stationary values of a general expression for the free energy of a system having a spatial variation in one of its scalar properties. We have shown that such an expression can be derived and that it is the integral of the sum of two contributions, one being a function only of the local value of the property and the other (the "gradient energy") a term which is proportional to the square of the local gradient. The minimum of this integral with respect to a one-dimensional composition or density variation corresponds to the free energy of a flat interface. The properties of the interface predicted by this treatment can be summarized as follows:

(1) The interface between two coexisting phases is diffuse and its thickness increases with increasing temperature until at the critical temperature (T_c) the interface is infinite in extent.

(2) In the critical region σ varies as $(T_c - T)^{1/2}$. This result is found to be in accord with experimental measurements.

(3) For a regular solution σ can be evaluated in terms of the molar volume, the critical temperature and a rms "interaction distance" (λ) which is a sensitive function of the intermolecular potentials. With a Lennard-Jones 6-12 potential the calculated and observed surface free energies of liquid Ne, Ar, N₂, and O₂ are in good agreement.

(4) The equation for the temperature dependence of σ of pure liquids is consistent with two well-known empirical expressions.

An additional interesting feature of our treatment (and one which is important to the nucleation theory) is the demonstration that σ is isotropic for a coherent interface in an unstrained cubic lattice. This is not the case for Becker's expression^{1(b)} because his interface was confined to a nonequilibrium configuration. And though the treatments of Ono⁵ and Hillert⁶ should give an isotropic σ , this fact was apparently not recognized because of their use of difference equations which could only be solved numerically. These equations were set up in terms of the interplanar spacing d and the fraction m of the number of nearest neighbors for a given atom which are in an adjacent plane. In our treatment this would correspond to setting $\lambda = (md^2)^{1/2}$. Thus even though m and d are individually dependent on the orientation, the factor $(md^2)^{1/2}$ which appears in the final expression for σ is invariant and for a nearest neighbor model is equal [from Eq. (3.10)] to $r_0/\sqrt{3}$, where r_0 is the radius of the first coordination shell. Physically, this means that the composition difference between successive planes will vary with orientation, but that the gradient relative to the lattice parameter remains constant.

In conclusion we should like to stress the limited applicability of our treatment. According to our basic assumptions the metastable free energy of the system must be a continuous function of the property concerned and, furthermore, the ratio of the maximum in this free energy function to the gradient energy coefficient κ must be small relative to the square of the intermolecular distance. If this latter requirement is not satisfied then, as will be seen from Eq. (2.23), there will be a steep gradient across the interface and it is then no longer justifiable to neglect derivatives higher than the second in deriving Eq. (2.1). We believe that in practice these conditions are likely to be satisfied only if there exists a critical point in the system or if one would have occurred but for the intervention of some other phase change, such as a eutectic.

A second and less obvious limitation (which also applies to all previous treatments) arises because we have only examined in detail the effect of a variation in a *single* property of the system. This suffices for a pure liquid surface where the only likely variable is density, and it is satisfactory for a binary liquid-liquid interface providing it can be assumed (a) that only the composition varies, the density remaining constant across the interface, or (b) that the gradient energy coefficient for the density variation is negligible compared with that for the composition variation. However, there are undoubtedly instances (such as at the surface of a binary liquid) where these conditions are not satisfied. The method of extending our treatment to cover the multiproperty case has been briefly indicated in a footnote.||

ACKNOWLEDGMENTS

We gratefully acknowledge the many helpful discussions we have had with C. P. Bean, E. W. Hart, D. S. Rodbell, G. W. Sears, and D. Turnbull. We are particularly indebted to R. Doremus and L. Guttman for their critical review of the manuscript.

We also wish to thank Mats Hillert of the Metallografiska Institutet, Stockholm, Sweden, for providing us with a copy of his thesis which initiated our interest in this subject.

APPENDIX

Symbols

A	Interface area (cm ²).
E	Intermolecular potential (erg).
N_0	Avogadro's number (6.022×10^{23} mole ⁻¹).
N_V	Number of molecules per unit volume (cm ⁻³).
T	Temperature (°K).
T_c	Critical or conjugate temperature (°K).
V_c	Critical volume (cm ³ mole ⁻¹).
V_m	Molar volume (cm ³ mole ⁻¹).
Z_n	Coordination number of n th shell.
F	Total free energy of system (erg).
c	Mole fraction of B component.
c_α, c_β	Equilibrium compositions.
c_c	Critical composition.
Δc	$(c - c_c)$.
f_0	Free energy per molecule of homogeneous solution (erg).
f_R	Free energy per molecule of a homogeneous regular solution (erg) [Eq. (3.1)].
Δf	Free energy per molecule referred to a standard state of an equilibrium two-phase mixture (erg) [Eq. (2.11)].
k	Boltzmann's constant (1.38×10^{-16} erg deg ⁻¹).
l	Thickness of interface (cm) [Eq. (2.25)].
r_n	Radius of n th coordination shell (cm).
r_0	Radius of first coordination shell or intermolecular distance (cm).
s	Entropy per molecule (erg deg ⁻¹).
u	Enthalpy per molecule (erg).
x	Distance (cm).
β, γ	Constants defined by Eqs. (2.17) and (2.18.)
ϵ	Dielectric constant.
κ	Gradient energy coefficient (erg cm ²).
λ	Interaction distance (cm) [Eq. (3.10)].
λ_0	Wavelength of light (cm).
μ	Chemical potential per molecule (erg).
$\mu(e)$	Chemical potential in coexisting phases (erg).
ν	$(E_{AB} - (1/2)(E_{AA} + E_{BB}))$ (erg).
$\rho(r)$	Reduced radial distribution function.
$\bar{\rho}$	Coefficient of ellipticity.
σ	Interfacial free energy (erg cm ⁻²) [Eq. (2.15)].
σ_r	Reduced interfacial free energy for a regular solution ($= \sigma_R / 2kT_c \lambda N_V$).
ω_n	$Z_n \nu_n$ (erg).