# Comparison of two free-energy expressions and their implications in surface enrichment

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We compare two free-energy expressions, developed by Cohen and Muthukumar [J. Chem. Phys. **90**, 5749 (1989)] and by Jerry and Nauman [J. Colloid Interface Sci. **154**, 122 (1992)], in terms of their predictions concerning surface enrichment. We show that a term must be added to the former expression so that it may predict the correct dependence of the surface composition on the bulk. The latter expression does predict the correct dependence. We have also derived the quadratic surface-energy contribution from a finite (nonzero) range interaction model.

The behavior of a binary mixture near a surface has attracted much attention in recent years. This interest has been fueled by new experimental techniques such as neutron reflectivity, secondary-ion mass spectroscopy, and nuclear-reaction analysis, which can accurately measure the concentration profile [1–5]. Resolutions of well under 100 nm have been reported, making possible a direct comparison between theory and experiment. A bounding wall, or even a vacuum, can cause the concentration of one component in a miscible mixture to be higher near the surface than in the bulk. Commonly called surface enrichment, this has been widely investigated [1–4]. In immiscible mixtures, the course of spinodal decomposition can be significantly altered near an interface; Jones et al. [6] observed composition waves propagating outward from the boundary, and their findings were supported by the theoretical work of Ball and Essery [7].

These same experimental methods have recently been applied to thin films, in which the influences of two surfaces affect the mixture [5,8,9]. In several of these studies, a composite film was formed by bringing together two individual thin films. Each of the thin films had a composition equal to one of the bulk coexistence concentrations. Concentration-profile measurements were recorded as the composite film equilibrated. Such an experimental design should be ideal for observing equilibrium phenomena such as the critical-temperature shift [10], wetting transitions [11], and the enrichment-depletion duality [10].

Theoretical studies of these phenomena have been based on the idea that the free energy of the mixture generally decreases with time and reaches a relative minimum at equilibrium. Given a mathematical expression for the free energy, an equilibrium concentration profile is often calculated by a minimization procedure. This profile may then be compared to the experimentally measured one. The free energy is a functional that depends on the concentration profile, and the general form may be written as

$$F = \int_0^\infty \left[ \Delta f(\phi) + \frac{\kappa}{2}(\phi_z)^2 \right] dz + \Phi(\phi_0, \phi_{z0}, \phi_{zz0}) , \quad (1)$$

with

$$\Delta f = f(\phi) - f(\phi_b) - f'(\phi_b)(\phi - \phi_b) , \quad (2)$$

where $F$ is the excess free energy of mixing, $f$ is the free energy of mixing for a uniform mixture, $z$ is the distance from the surface, and $\kappa$ is the gradient energy parameter. The volume fraction is denoted $\phi$, with $\phi_b$ and $\phi_0$ being the bulk and surface values, respectively. The derivative of $f$ with respect to $\phi$ is written $f'$, and differentiation with respect to distance is denoted by the subscript $z$. The surface contribution to the free energy is written as $\Phi$, and may depend on the surface concentration and higher derivatives as well.

Obviously, the particular functional form of $\Phi$ is important. In Cahn's pioneering work [12], $\Phi$ was assumed to be a function of only one variable $\phi_0$. He used variational calculus to write the governing differential equation and boundary condition for the equilibrium concentration profile. He did not specify a particular functional form for $\Phi(\phi_0)$, which is necessary if one wishes to solve the differential equation. Later, others such as Schmidt and Binder [13] used a quadratic expression for $\Phi(\phi_0)$. The quadratic expression is essentially phenomenologically based. However, the form is supported by a simple direct-contact molecular-interaction model as shown in [10].

Improvements in the quadratic approximation were achieved by two investigations [14,15]. Both derived a complete free-energy expression from first principles. The analysis in [15] was based on the partition function, and a modified Debye model was used in [14]. The findings were similar in that $\Phi$ was found to be a function of not only $\phi_0$, but the first and second derivatives as well. The specific functional forms in [14] and [15] differ, and we will compare their physical implications in surface enrichment.

Part of the motivation for this work is to improve the correspondence between theory and experiment. Observations of "surface flattening" in [3] indicate that the quadratic approximation might be inadequate for calculating the profile very close to the surface. In addition, these alternative free-energy expressions might provide information on equilibrium interfacial phenomena, such as wetting, which cannot be provided by a simple quadratic approximation.

When $\Phi$ does have a derivative dependence, the standard variational-calculus technique cannot be used to

determine the equilibrium profile. The reason was explained in [16]; in order for the variation of the free energy to be zero, the equilibrium profile would have to satisfy a first-order differential equation with three boundary conditions. As shown in [16], the equilibrium profile has discontinuities in $\phi_z$ and $\phi_{zz}$ at $z=0$. It is these discontinuities that are responsible for the apparent overspecification of the problem. A modified variational-calculus method, which can accommodate discontinuities, was developed in [16]. The three boundary conditions were written as

$$\Phi_\phi(\phi_0,\phi_{z0},\phi_{zz0})-\kappa\phi_{z0^+}=0 \ , \tag{3}$$

$$\Phi_{\phi z}(\phi_0,\phi_{z0},\phi_{zz0})=0 \ , \tag{4}$$

$$\Phi_{\phi zz}(\phi_0,\phi_{z0},\phi_{zz0})=0 \ , \tag{5}$$

where the subscripts $\phi$, $\phi z$, and $\phi zz$ indicate a partial derivative with respect to $\phi$, $\phi_z$, and $\phi_{zz}$, respectively. The subscript $0^+$ indicates evaluation at $z=0^+$. The values of $\phi_{z0^+}$ and $\phi_{z0}$ are different due to the jump in $\phi_z$ at the boundary. The three conditions must be satisfied so that the variation of $F$ is zero, which is a necessary condition for the concentration profile to be at a free-energy minimum.

The governing differential equation is the same regardless of the particular functional form of $\Phi$. However, the boundary conditions are different. In what follows, we will apply conditions (3)–(5) to each $\Phi$ expression and investigate the physical consequences. Before doing this, however, we can make some general observations. The concentration is continuous at $z=0$, $\phi_{0^+}=\phi_0$, but the derivatives are not: $\phi_{z0^+}\neq\phi_{z0}$ and $\phi_{zz0^+}\neq\phi_{zz0}$. Therefore, there are two additional variables, $\phi_{z0}$ and $\phi_{zz0}$. The differential equation is first order and applies for $z>0$. To solve this equation, only one boundary condition is needed, and this is provided by Eq. (3). Unfortunately, Eq. (3) also contains $\phi_{z0}$ and $\phi_{zz0}$ terms, which are auxiliary variables. They may be eliminated by a simultaneous solution of Eqs. (4) and (5), which provides a way of expressing $\phi_{z0}$ and $\phi_{zz0}$ in terms of $\phi_0$. As will soon become evident, the specific form of $\Phi$ will affect Eqs. (3)–(5), and can dramatically influence the qualitative predictions on surface enrichment.

The Cohen and Muthukumar (CM) $\Phi$ expression can be written as

$$\Phi(\phi,\phi_z,\phi_{zz})=D_1\phi+E_1\phi\ln\phi+G_1(1-\phi)\ln(1-\phi)$$
$$+[H_1\ln\phi+J_1\ln(1-\phi)]\phi_z$$
$$+\left[\frac{L_1}{\phi}+\frac{Q_1}{1-\phi}\right](\phi_z)^2$$
$$+[T_1\ln\phi+R_1\ln(1-\phi)]\phi_{zz} \ , \tag{6}$$

where the coefficients $D_1$ through $T_1$ were defined in the original publication [15]. In Ref. [17], Eq. (6) was substituted in conditions (3)–(5), and the equilibrium surface concentration $\phi_0$ was found to be independent of the bulk concentration $\phi_b$. Experiments [1] have demonstrated that the surface concentration does depend on the bulk.

The inconsistency arises from the form of the CM expression. Upon differentiation, Eq. (6) yields

$$\Phi_{\phi zz}=T_1\ln\phi+R_1\ln(1-\phi) \ . \tag{7}$$

To satisfy the third boundary condition, Eq. (7) must be set to zero. This indicates that $\phi_0$ only depends on $T_1$ and $R_1$. In order for the surface composition to depend on the bulk, $\Phi_{\phi zz}$ must be a function of $\phi_z$ and/or $\phi_{zz}$. This would be the case if CM contained a $\phi_{zz}^2$ term, or if the coefficient of their $\phi_{zz}$ term contained a $\phi_z$ dependence.

The Jerry and Nauman (JN) $\Phi$ expression may be written as

$$\Phi(\phi,\phi_z,\phi_{zz})=D\phi+E\phi^2+G\phi_z+H(\phi_z)^2+J\phi\phi_z$$
$$+L\phi_{zz}+Q(\phi_{zz})^2+T\phi\phi_{zz}+R \ . \tag{8}$$

The parameters $D$ through $T$ were defined in [14]. They are all related to the intermolecular interaction-energy functions $e_{ij}(r)$, where $r$ is the distance separating two molecules and $e_{ij}$ is the interaction energy. The subscript $ij$ can represent an interaction between two molecules of the mixture or between a mixture and a wall molecule. Actually, $D$ through $T$ do not depend on the $e_{ij}$ functions directly, but rather on spatially weighted integrals of these functions. All the parameters in $\Phi$ can be estimated by using an approximation, such as the Lennard-Jones potential, for $e_{ij}(r)$. Not all the parameters are independent; note that $J$ is exactly equal to $\kappa/2$, where $\kappa$ is just the gradient energy parameter. The derivation may be found in [18].

After the JN expression is included in Eqs. (3)–(5), we find

$$D+2E\phi_0+J\phi_{z0}+T\phi_{zz0}-\kappa\phi_{z0^+}=0 \ , \tag{9}$$

$$G+2H\phi_{z0}+J\phi_0=0 \ , \tag{10}$$

$$L+2Q\phi_{zz0}+T\phi_0=0 \ . \tag{11}$$

Equations (10) and (11) can be solved for $\phi_{z0}$ and $\phi_{zz0}$, respectively, and then substituted into Eq. (9) to give

$$\left[D-\frac{GJ}{2H}-\frac{TL}{2Q}\right]+\left[2E-\frac{J^2}{2H}-\frac{T^2}{2Q}\right]\phi_0-\kappa\phi_{z0^+}=0 \ . \tag{12}$$

In this case, the surface concentration does depend on the bulk value, through $\phi_{z0^+}$. Equation (12) can also be written

$$-\mu_1-g\phi_0-\kappa\phi_{z0^+}=0 \ , \tag{13}$$

with

$$\mu_1=\frac{GJ}{2H}+\frac{TL}{2Q}-D \ , \tag{14}$$

$$g=\frac{T^2}{2Q}+\frac{J^2}{2H}-2E \ . \tag{15}$$

Here, we have associated the coefficients of the JN expression with the coefficients of the conventional

derivative-free model $\Phi_S$:

$$\Phi_S(\phi) = -\mu_1\phi - \tfrac{1}{2}g\phi^2 . \tag{16}$$

Let us call $\phi_J(z)$ the extremal profile when the JN expression is used as the surface-energy expression, and let $\phi_S(z)$ be the extremal profile when $\Phi_S$ is used. Since $\Phi_S$ is derivative free, there are no discontinuities at $z=0$, and the standard variational-calculus techniques apply. The boundary condition for $\phi_S(z)$ is

$$\kappa\phi_{z0} = \frac{d\Phi_S}{d\phi}(\phi_0) . \tag{17}$$

From Eqs. (13), (16), and (17), it is clear that $\phi_S$ and $\phi_J$ satisfy nearly the same boundary condition and differential equation. Therefore, for $z>0$, $\phi_J(z)=\phi_S(z)$. At $z=0$, $\phi_J$ is continuous and therefore $\phi_J(0)=\phi_S(0)$. The values of the first and second derivatives of $\phi_J$ are discontinuous, but may be calculated by substituting $\phi_S(0)$ for $\phi_0$ in Eqs. (10) and (11) and solving for $\phi_{z0}$ and $\phi_{zz0}$, respectively. This finding is interesting because it indicates that the conventional quadratic expression is more significant than just a phenomenological approximation. In fact, the JN expression should predict exactly the same profile as the quadratic. The only difference is the derivative jumps at the boundary. At this time, it is difficult to say whether the discontinuities are artifacts of the mathematics or whether they represent something more physically meaningful. Perhaps, the jump in the first derivative may be a precursor to the "surface-flattening" effect that was reported in [3].

The temperature dependence of all the parameters in the JN expression was reported in [14]. Using this information along with Eqs. (14) and (15), we conclude that both $\mu_1$ and $g$ vary as the inverse temperature. In addition, the ratio $\mu_1/g$ should be relatively independent of temperature. A simple direct-contact interaction model [10] can predict the same dependence. Jones et al. [1]

calculated values of $\mu_1$ and $g$ from data obtained by forward-recoil spectrometry. However, their data were reported at a single temperature. Currently, we do not know of anyone who has measured the temperature dependence of these parameters.

The CM expression does include the surface entropic terms $E_1\phi\ln\phi$ and $G_1(1-\phi)\ln(1-\phi)$. These arise due to the influence of the surface on the entropy of the polymer mixture. The presence of a surface reduces the number of possible configurations available to the polymer molecules. The JN expression does not include the surface effect on the entropy. This effect should be small for mixtures consisting of two polymers having nearly the same molecular weight.

One might expect $E_1$ and $G_1$ to approach zero as the degree of polymerization decreases, and the surface entropic effect should be negligible for a monomer mixture. It is in this limit that the CM and JN expressions should be compared. Then, there is only one derivative-free term in CM, namely $D_1\phi$. To be consistent with JN, the CM expression should also contain a $\phi^2$ term.

In the derivation of JN [14], interactions between the individual mixture and wall molecules were treated in the same way as the interactions between the mixture molecules themselves. This is in contrast to the short-ranged ($\delta$-function) surface interaction that was assumed in the derivation of CM. We have shown that the conventional, derivative-free quadratic expression for $\Phi$ should make essentially the same predictions for equilibrium surface behavior as JN. Apparently, the wall-mixture interaction range must be substantially larger than that considered in JN in order to see "long-range" effects. To model this type of behavior, the integral term in the free energy would have to be modified to include the long-range interactions. A phenomenological approach along these lines has been reported in [19]. A derivation of such a free-energy expression from first principles has not yet been performed.

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[1] R. A. L. Jones, E. J. Kramer, M. H. Rafailovich, J. Sokolov, and S. A. Schwarz, Phys. Rev. Lett. 62, 280 (1989).

[2] X. Zhao, W. Zhao, J. Sokolov, M. H. Rafailovich, S. A. Schwarz, B. J. Wilkens, R. A. L. Jones, and E.J. Kramer, Macromolecules 24, 5991 (1991).

[3] R. A. L. Jones, L. J. Norton, E. J. Kramer, R. J. Composto, R. S. Stein, T. P. Russell, A. Mansour, A. Karim, G. P. Felcher, M. H. Rafailovich, J. Sokolov, X. Zhao, and S. A. Schwarz, Europhys. Lett. 12, 41 (1990).

[4] R. A. L. Jones and E. J. Kramer, Philos. Mag. B 62, 129 (1990).

[5] U. Steiner, J. Klein, E. Eiser, A. Budkowski, and L. J. Fetters, Science 258, 1126 (1992).

[6] R. A. L. Jones, L. J. Norton, E. J. Kramer, F. S. Bates, and P. Wiltzius, Phys. Rev. Lett. 66, 1326 (1991).

[7] R. C. Ball and R. L. H. Essery, J. Phys.: Condens. Matter 2, 10 303 (1990).

[8] A. Budkowski, U. Steiner, and J. Klein, J. Chem. Phys. 97, 5229 (1992).

[9] F. Bruder and R. Brenn, Phys. Rev. Lett. 69, 624 (1992).

[10] R. A. Jerry and E. B. Nauman, Phys. Lett. A 167, 198 (1992).

[11] P. G. de Gennes, Rev. Mod. Phys. 57, 827 (1985).

[12] J. W. Cahn, J. Chem. Phys. 66, 3667 (1977).

[13] I. Schmidt and K. Binder, J. Phys. (Paris) 46, 1631 (1985).

[14] R. A. Jerry and E. B. Nauman, J. Colloid Interface Sci. 154, 122 (1992).

[15] S. M. Cohen and M. Muthukumar, J. Chem. Phys. 90, 5749 (1989).

[16] R. A. Jerry and E. B. Nauman (unpublished).

[17] R. A. Jerry and E. B. Nauman, J. Chem. Phys. 97, 7829 (1992).

[18] R. A. Jerry, Ph.D. thesis, Rensselaer Polytechnic Institute, 1992, p. 76.

[19] Z. Y. Chen, J. Noolandi, and D. Izzo, Phys. Rev. Lett. 66, 727 (1991).