Diffusion Equation for Interacting Particles

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A new approach to molecular diffusion is developed using density functionals for fluxes and the Metropolis algorithm in the mass balance equation. This procedure results in a new equation for diffusion of interacting particles which has multiple solutions and gives density distributions for coexisting and metastable phases. It is shown that the diffusion of interacting molecules is driven by two variables: the density gradient of molecules and the density of molecule−vacancy pairs ("pseudoparticles").

Introduction

Diffusion is an important phenomenon in the field of physical chemistry and in many applications including membrane separations, chromatography, extraction, catalysis, metallurgy, and semiconductor technology.[1−14] Diffusion has been studied in gases[1] and liquids[2] as well as in porous and crystalline solids.[1,3] Classical studies have been done on diffusion in semiconductors,[4] metals and alloys,[5] polymers,[6] and various fluids.[7] Special methods have been developed for the diffusion of reactive molecules[8] and for quantum mechanical systems.[9] Modern theories of diffusion consider sophisticated conditions, including fractal dimensions, disordered lattices, and the diffusion of complex molecules (such as proteins).[10]

Modeling diffusion has been most successful for systems where intermolecular interactions are weak and where the interactions do not result in phase transitions.[11−14] If interactions are important and phase transitions are possible, modeling diffusion becomes significantly harder and there are no standardized methods that provide reliable predictive capabilities.[1−8]

Recently, Giacomin, Lebowitz, and Marra (GLM)[15−17] developed a rigorous statistical mechanical theory of nonequilibrium phase transitions. The GLM theory provides a fundamental theoretical background for modeling the evolution of nonequilibrium coexisting phases.

In this paper, we derive a partial differential equation for the diffusion of interacting particles by considering the grid form of this equation and write density functionals for fluxes using the Metropolis algorithm. (Note that this algorithm is commonly used to define frequencies of moves up and down energy gradients in dynamic Monte Carlo simulations.) This procedure gives an equation for diffusion that is consistent with the GLM theory in the hydrodynamic limit and predicts diffusion in systems with phase transitions.

Diffusion Equation

For fluids, the fundamental form[14] of the diffusion equation can be written in terms of the normalized density,[15] ρ,

$$\frac{1}{D}\frac{\partial \rho}{\partial t} = \frac{\partial^2 \rho}{\partial x^2} + \frac{\partial^2 \rho}{\partial y^2} + \frac{\partial^2 \rho}{\partial z^2} \tag{1}$$

where D is the diffusion coefficient; t is time; x, y, and z are Cartesian coordinates; and $0 \leq \rho \leq 1$.

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There are various generalizations of eq 1, such as the Fokker−Planck equation[18] and its modern modifications.[19,20] Generally, the diffusion equation should take into account motion of the medium, chemical reactions, convection, temperature gradients, external fields, and various intermolecular interactions, resulting in a variety of phenomena which accompany diffusion.[1−14] In addition to the core terms given by eq 1, a more general model may include nonlinearities relating the time derivative of density with first and second derivatives of density with respect to position coordinates:

$$\frac{1}{D}\frac{\partial \rho}{\partial t} = \Psi\left[\frac{\partial^2 \rho}{\partial x^2}, \frac{\partial^2 \rho}{\partial y^2}, \frac{\partial^2 \rho}{\partial z^2}, \frac{\partial \rho}{\partial x}, \frac{\partial \rho}{\partial y}, \frac{\partial \rho}{\partial z}, \rho\right] \tag{2}$$

Equation 2 can be discretized and written in the form of finite differences:

$$\frac{1}{D}\frac{\partial \rho_{i,j,k}}{\partial t} \approx \Psi\left[\frac{(\rho_{i+1,j,k} - \rho_{i,j,k}) - (\rho_{i,j,k} - \rho_{i-1,j,k})}{\delta^2},\right.$$
$$\frac{(\rho_{i,j+1,k} - \rho_{i,j,k}) - (\rho_{i,j,k} - \rho_{i,j-1,k})}{\delta^2},$$
$$\frac{(\rho_{i,j,k+1} - \rho_{i,j,k}) - (\rho_{i,j,k} - \rho_{i,j,k-1})}{\delta^2},$$
$$\left.\frac{(\rho_{i+1,j,k} - \rho_{i,j,k})}{\delta}, \frac{(\rho_{i,j+1,k} - \rho_{i,j,k})}{\delta}, \frac{(\rho_{i,j,k+1} - \rho_{i,j,k})}{\delta}, \rho_{i,j,k}\right] \tag{3}$$

In the limit of small δ, eq 3 turns into eq 2. However, we will assume that eq 3 not only has mathematical meaning but also describes the mass balance in an (i,j,k) network where fluxes from site to site are driven thermodynamically. In other words, there is an imaginary cubic lattice where molecules can sit on sites (i,j,k), and $\rho_{i,j,k}$ is the probability of site (i,j,k) being occupied. Therefore, eq 3 can be written in the following form:[21]

$$\frac{1}{D}\frac{\partial \rho_{i,j,k}}{\partial t} \approx K(f_{i+1,j,k}^+ - f_{i+1,j,k}^- + f_{i-1,j,k}^+ - f_{i-1,j,k}^- + f_{i,j+1,k}^+ -$$
$$f_{i,j+1,k}^- + f_{i,j-1,k}^+ - f_{i,j-1,k}^- + f_{i,j,k+1}^+ - f_{i,j,k+1}^- + f_{i,j,k-1}^+ - f_{i,j,k-1}^-) \tag{4}$$

where f^+ and f^- are fluxes coming into site (i,j,k) and coming out of site (i,j,k) and K determines the units of the fluxes.

Note that viewing eq 3 as an equation for an imaginary lattice does not reduce our model to a lattice system, nor does the

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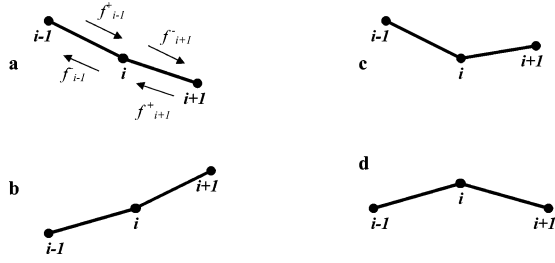*J. Phys. Chem. B, Vol. 109, No. 33, 2005* **16063**

Figure 1. Energy profiles in the *i* direction: (a) $H_{i-1,j,k} > H_{i,j,k} > H_{i+1,j,k}$; (b) $H_{i+1,j,k} > H_{i,j,k} > H_{i-1,j,k}$; (c) $H_{i-1,j,k} > H_{i,j,k}$ and $H_{i+1,j,k} > H_{i,j,k}$; (d) $H_{i,j,k} > H_{i-1,j,k}$ and $H_{i,j,k} > H_{i+1,j,k}$.

assumption of the finite difference form (eq 3) for eq 2. However, considering eq 3 in the form of eq 4 will lead to a continuous equation in the limit of small δ. In this paper, we first derive the finite difference form (eq 4), then go to the form of eq 3, and, finally, consider the limit of small δ to obtain eq 2. This procedure results in an equation for diffusion of interacting particles consistent with the theory of Giacomin, Lebowitz, and Marra[15−17] in the hydrodynamic limit; that is, it gives a configurational energy term, div$[\rho(1 - \rho)$ grad $H]$, in addition to classical terms of eq 1 for systems with a nonzero gradient of the configurational energy, H.

To derive the f^+ and f^- terms of eq 4, we use the normalized density, $\rho(i,j,k)$, defined as the probability that site (i,j,k) is occupied (similar to lattice theories[22−24]) and Metropolis probabilities.[25]

Metropolis Principle in Density Functionals for Fluxes

Consider fluxes in the *i* direction between site (i,j,k) and its neighbors, $(i+1,j,k)$ and $(i−1,j,k)$. The Metropolis probability, *Pr*, of accepting moves in dynamic Monte Carlo simulations depends on the configurational energy change, ΔH:[26] if $\Delta H < 0$, *Pr* is unity; if $\Delta H > 0$, *Pr* is proportional to Boltzmann's factor. To illustrate, we consider four different energy profiles, $H_{i,j,k}$, between points $(i+1,j,k)$ and $(i−1,j,k)$; see Figure 1. It is necessary to consider these four profiles because the Metropolis algorithm gives different fluxes for them. Note that, in the following equations, H is normalized by k_BT where k_B is Boltzmann's constant and T is the absolute temperature.

Fluxes $f^+_{i+1,j,k}$, $f^-_{i+1,j,k}$, $f^+_{i−1,j,k}$ and $f^-_{i−1,j,k}$ for eq 4 can be written in the following form:

$$f^+_{i+1,j,k} = \frac{1}{z_0}\rho_{i+1,j,k}(1 - \rho_{i,j,k})\lambda_{i,j,k} \quad (5)$$

$$f^-_{i+1,j,k} = \frac{1}{z_0}\rho_{i,j,k}(1 - \rho_{i+1,j,k})\lambda_{i,j,k}\exp(H_{i,j,k} - H_{i+1,j,k}) \quad (6)$$

$$f^+_{i−1,j,k} = \frac{1}{z_0}\rho_{i−1,j,k}(1 - \rho_{i,j,k})\lambda_{i−1,j,k}\exp(H_{i−1,j,k} - H_{i,j,k}) \quad (7)$$

$$f^-_{i−1,j,k} = \frac{1}{z_0}\rho_{i,j,k}(1 - \rho_{i−1,j,k})\lambda_{i−1,j,k} \quad (8)$$

where $\lambda_{i,j,k} = \min[1, \exp(H_{i+1,j,k} - H_{i,j,k})]$ and z_0 is the coordination number (number of neighboring sites);[22,23] for cubic and square lattices, $z_0 = 6$ and $z_0 = 4$, respectively, and for the one-dimensional case, $z_0 = 2$.

Note that the factor $\rho_{i+1,j,k}(1 - \rho_{i,j,k})$ in eq 5 is the probability of having a molecule on site $(i+1,j,k)$ and site (i,j,k) being empty. Similar factors are in eqs 6−8. Thus, a molecule has a chance to move from site 1 to site 2 if it is available on site 1 and if site 2 is empty. The factor $1/z_0$ adjusts the probability of

moving from site 1 for the number of neighboring sites. The factors $\exp(H_{i+1,j,k} - H_{i,j,k})$ in eqs 5−8 are Metropolis probabilities of acceptance when a molecule moves up the energy gradient; these factors disappear where a molecule moves down the energy gradient. Thus, eqs 5−8 reflect the energy profiles in Figure 1 and show differences in fluxes for different profiles due to the Metropolis algorithm.

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To avoid cumbersome notation, consider the one-dimensional case which easily can be generalized for two and three dimensions. Plugging eqs 5−8 into the one-dimensional version of eq 4 gives for profile a in Figure 1

$$\frac{1}{D}\frac{\partial \rho_i}{\partial t} \approx \frac{K}{z_0}[\rho_{i+1}(1 - \rho_i)\exp(H_{i+1} - H_i) - \rho_i(1 - \rho_{i+1}) + \rho_{i-1}(1 - \rho_i) - \rho_i(1 - \rho_{i-1})\exp(H_i - H_{i-1})] \quad (9)$$

Consider the following expansions:

$$\rho_{i+1} = \rho_i + \frac{\partial \rho_i}{\partial x}\delta + \frac{1}{2}\frac{\partial^2 \rho_i}{\partial x^2}\delta^2 + o(\delta^3) \quad (10)$$

$$\rho_{i-1} = \rho_i - \frac{\partial \rho_i}{\partial x}\delta + \frac{1}{2}\frac{\partial^2 \rho_i}{\partial x^2}\delta^2 + o(\delta^3) \quad (11)$$

$$H_{i+1} = H_i + \frac{\partial H_i}{\partial x}\delta + \frac{1}{2}\frac{\partial^2 H_i}{\partial x^2}\delta^2 + o(\delta^3) \quad (12)$$

$$H_{i-1} = H_i - \frac{\partial H_i}{\partial x}\delta + \frac{1}{2}\frac{\partial^2 H_i}{\partial x^2}\delta^2 + o(\delta^3) \quad (13)$$

where $\partial \rho_i/\partial x$ is $\partial \rho(x)/\partial x$ at $x = i$, $\partial^2 \rho_i/\partial x^2$ is $\partial^2 \rho(x)/\partial x^2$ at $x = i$, $\partial H_i/\partial x$ is $\partial H(x)/\partial x$ at $x = i$, and $\partial^2 H_i/\partial x^2$ is $\partial^2 H(x)/\partial x^2$ at $x = i$. Plugging ρ_{i+1}, ρ_{i-1}, H_{i+1}, and H_{i-1} from eqs 10−13 into eq 9 gives, after algebraic manipulations,

$$\frac{1}{D}\frac{\partial \rho_i}{\partial t} \approx \frac{K}{z_0}\left[\frac{\partial^2 \rho_i}{\partial x^2} + (1 - 2\rho_i)\frac{\partial \rho_i}{\partial x}\frac{\partial H_i}{\partial x} + \rho_i(1 - \rho_i)\frac{\partial^2 H_i}{\partial x^2}\right]\delta^2 + o(\delta^3) \quad (14)$$

Note that the linear term (with respect to δ) cancels and the first meaningful term is quadratic; the symbol $o(\delta^3)$ denotes cubic and higher terms.

Comparison of eq 14 with eqs 1−3 indicates that $K = z_0/\delta^2$ and the original continuous equation is

$$\frac{1}{D}\frac{\partial \rho}{\partial t} = \frac{\partial^2 \rho}{\partial x^2} + (1 - 2\rho)\frac{\partial \rho}{\partial x}\frac{\partial H}{\partial x} + \rho(1 - \rho)\frac{\partial^2 H}{\partial x^2} \quad (15)$$

For profile b in this figure, plugging eqs 5−8 into eq 4 gives instead of eq 9

$$\frac{1}{D}\frac{\partial \rho_i}{\partial t} \approx \frac{K}{z_0}[\rho_{i+1}(1 - \rho_i) - \rho_i(1 - \rho_{i+1})\exp(H_i - H_{i+1}) + \rho_{i-1}(1 - \rho_i)\exp(H_{i-1} - H_i) - \rho_i(1 - \rho_{i-1})] \quad (16)$$

For profile c, eqs 5−8 plugged into eq 4 give

$$\frac{1}{D}\frac{\partial \rho_i}{\partial t} \approx \frac{K}{z_0}[\rho_{i+1}(1 - \rho_i) - \rho_i(1 - \rho_{i+1})\exp(H_i - H_{i+1}) + \rho_{i-1}(1 - \rho_i) - \rho_i(1 - \rho_{i-1})\exp(H_i - H_{i-1})] \quad (17)$$

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and for profile d, using eqs 5−8 in eq 4 results in

$$\frac{1}{D}\frac{\partial \rho_i}{\partial t} \approx \frac{K}{z_0}[\rho_{i+1}(1-\rho_i)\exp(H_{i+1}-H_i) - \rho_i(1-\rho_{i+1}) +$$
$$\rho_{i-1}(1-\rho_i)\exp(H_{i-1}-H_i) - \rho_i(1-\rho_{i-1})] \quad (18)$$

Using expansions 10−13 in eq 16 gives, after algebraic manipulations, eq 14. Thus, profiles a and b in Figure 1 give the same equations of diffusion.

Using expansions 10−13 in eqs 17 and 18 gives, after algebraic manipulations, the following equations instead of eq 14:

$$\frac{1}{D}\frac{\partial \rho_i}{\partial t} \approx \frac{K}{z_0}\left\{\frac{\partial^2 \rho_i}{\partial x^2} + (1-2\rho_i)\frac{\partial \rho_i}{\partial x}\frac{\partial H_i}{\partial x} + \rho_i(1-\rho_i)\frac{\partial^2 H_i}{\partial x^2} - \right.$$
$$\left.\frac{\partial H_i}{\partial x}\left[\frac{\partial \rho_i}{\partial x} + \rho_i(1-\rho_i)\frac{\partial H_i}{\partial x}\right]\right\}\delta^2 + o(\delta^3) \quad (19)$$

for profile c and

$$\frac{1}{D}\frac{\partial \rho_i}{\partial t} \approx \frac{K}{z_0}\left\{\frac{\partial^2 \rho_i}{\partial x^2} + (1-2\rho_i)\frac{\partial \rho_i}{\partial x}\frac{\partial H_i}{\partial x} + \rho_i(1-\rho_i)\frac{\partial^2 H_i}{\partial x^2} + \right.$$
$$\left.\frac{\partial H_i}{\partial x}\left[\frac{\partial \rho_i}{\partial x} + \rho_i(1-\rho_i)\frac{\partial H_i}{\partial x}\right]\right\}\delta^2 + o(\delta^3) \quad (20)$$

for profile d.

As seen from eqs 19 and 20, profiles c and d have an extra term, $\pm(\partial H_i/\partial x)[(\partial \rho_i/\partial x) + \rho_i(1-\rho_i)(\partial H_i/\partial x)]$, compared to eq 14. However, this occurs only at local maxima or minima of H_i; therefore, at these points, the term $\pm(\partial H_i/\partial x)[(\partial \rho_i/\partial x) + \rho_i(1-\rho_i)(\partial H_i/\partial x)]$ equals zero. Thus, eqs 14 and 15 are universal in terms of profiles a−d.

Since $1-2\rho = \partial[\rho(1-\rho)]/\partial\rho$, eq 15 can be rewritten in the following compact form:

$$\frac{1}{D}\frac{\partial \rho}{\partial t} = \frac{\partial^2 \rho}{\partial x^2} + \frac{\partial}{\partial x}\left[\rho(1-\rho)\frac{\partial H}{\partial x}\right] \quad (21)$$

The three-dimensional version of this equation is

$$\frac{1}{D}\frac{\partial \rho}{\partial t} = \frac{\partial^2 \rho}{\partial x^2} + \frac{\partial^2 \rho}{\partial y^2} + \frac{\partial^2 \rho}{\partial z^2} + \frac{\partial}{\partial x}\left[\rho(1-\rho)\frac{\partial H}{\partial x}\right] + \frac{\partial}{\partial y}\left[\rho(1-\right.$$
$$\left.\rho)\frac{\partial H}{\partial y}\right] + \frac{\partial}{\partial z}\left[\rho(1-\rho)\frac{\partial H}{\partial z}\right] \quad (22)$$

Note that eqs 21 and 22 are consistent with the GLM theory[15−17] because the energy terms, $(\partial/\partial x)[\rho(1-\rho)(\partial H/\partial x)] + (\partial/\partial y)[\rho(1-\rho)(\partial H/\partial y)] + (\partial/\partial z)[\rho(1-\rho)(\partial H/\partial z)]$, coincide with those derived by Giacomin and Lebowitz in the hydrodynamic limit.[16]

Steady-State Solution

If H does not depend on density or on coordinates, eq 22 turns into eq 1. When $H = H(\rho,x,y,z)$, eq 22 predicts nonequilibrium behavior of interacting particles.

To illustrate the physics embedded in this equation, consider its

simplest, one-dimensional version given by eq 21. The steady-state case with $\partial \rho/\partial t = 0$ gives from eq 21

$$\frac{\partial \rho}{\partial x} + \rho(1-\rho)\frac{\partial H}{\partial x} = \text{constant} = C_1 \quad (23)$$

It can be shown that this first integral (constant C_1) defines the

total flux through the system. Consider the total flux, F_t, as $DK\delta$ $(f_{i+1,j,k}^- - f_{i+1,j,k}^+)$; with eqs 5−8, it gives

$$F_t = \frac{DK}{z_0}[\rho_{i,j,k}(1-\rho_{i+1,j,k}) - \rho_{i+1,j,k}(1-\rho_{i,j,k})\exp(H_{i+1,j,k} -$$
$$H_{i,j,k})]\delta \quad (24)$$

(Note that considering F_t as $DK\delta(f_{i+1,j,k}^- - f_{i+1,j,k}^+)$ is consistent with Einstein's formula for Brownian motion,[12] $\delta^2 = z_0 D\tau$, with some characteristic microscopic time, τ; since $K = z_0/\delta^2$ and $Dz_0 = \delta^2/\tau$, then $DK\delta = \delta/\tau$.)

Using expansions 10−13 in eq 24, after algebraic manipulations, results in

$$F_t = -\frac{DK}{z_0}\left\{\left[\frac{\partial \rho}{\partial x} + \rho_i(1-\rho_i)\frac{\partial H_i}{\partial x}\right]\delta^2 + o(\delta^3)\right\} \quad (25)$$

With $K = z_0/\delta^2$, eq 25 gives

$$F_t = -D\left[\frac{\partial \rho_i}{\partial x} + \rho_i(1-\rho_i)\frac{\partial H_i}{\partial x}\right] \quad (26)$$

Thus, $F_t = -DC_1$.

If there is no external field (H does not depend on x explicitly), $H = H(\rho)$ and eq 23 can be written as

$$\frac{\partial \rho}{\partial x} + \rho(1-\rho)\frac{\partial H}{\partial \rho}\frac{\partial \rho}{\partial x} = C_1 \quad (27)$$

or

$$d\rho\left[1 + \rho(1-\rho)\frac{\partial H}{\partial \rho}\right] = C_1\,dx \quad (28)$$

Integration of eq 28 gives the general solution

$$\rho + \int \rho(1-\rho)\frac{\partial H}{\partial \rho}\,d\rho = C_1 x + C_2 \quad (29)$$

where C_1 and C_2 are arbitrary constants to be determined from boundary conditions.

Mean-Field Example

With no external field, $H = H(\rho)$. The simplest particular case is for H to be a linear function of ρ:

$$H(\rho) = \frac{z_0\epsilon}{k_B T}\rho \quad (30)$$

in the mean-field approximation[22−24] where ϵ is the energy of interactions between nearest neighbors. Plugging $H(\rho)$ from eq 30 into eq 23 gives

$$\frac{\partial \rho}{\partial x} + \frac{z_0\epsilon\rho(1-\rho)}{k_B T}\frac{\partial \rho}{\partial x} = C_1 \quad (31)$$

which can be rewritten as

$$\rho(1-\rho)\frac{\partial}{\partial x}\left(\ln\frac{\rho}{1-\rho} + \frac{z_0\epsilon}{k_B T}\rho\right) = C_1 \quad (32)$$

Since $DC_1 = -F_t$ and $\ln[\rho/(1-\rho)] + [(z_0\epsilon/k_B T)\rho]$ is the mean-

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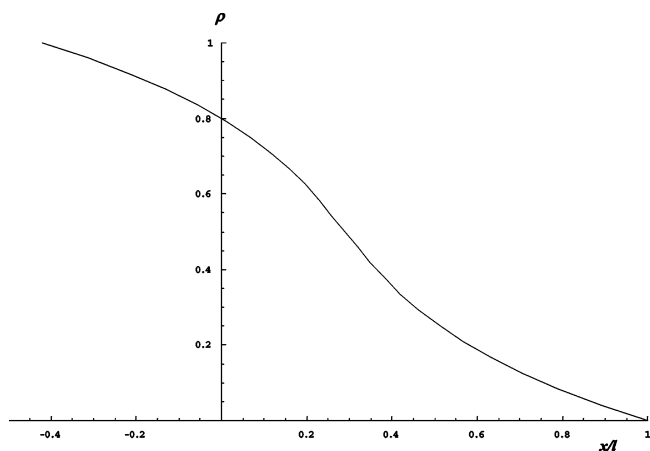*J. Phys. Chem. B, Vol. 109, No. 33, 2005* **16065**

Figure 2. Density distribution for $\rho_0 = 0.8$, $\rho_l = 0$, and a supercritical temperature of $z_0\epsilon/k_BT = -3$.

field chemical potential,[24] μ, then

$$F_t = -D\rho(1 - \rho)\frac{\partial\mu}{\partial x} \tag{33}$$

Note that D and ϵ in eqs 31 and 33 are independent of density.
   Equation 31 can be transformed into

$$d\rho\left[1 + \frac{z_0\epsilon}{k_BT}\rho(1 - \rho)\right] = C_1\,dx \tag{34}$$

and, after its integration, into

$$\rho + \frac{z_0\epsilon}{k_BT}\left(\frac{\rho^2}{2} - \frac{\rho^3}{3}\right) = C_1x + C_2 \tag{35}$$

To analyze the physics predicted by eq 35, consider diffusion between points $x = 0$ and $x = l$ with the following boundary conditions:

$$\rho = \rho_0 \text{ at } x = 0 \tag{36a}$$

$$\rho = \rho_l \text{ at } x = l \tag{36b}$$

Using these conditions for eq 35 gives

$$\frac{x}{l} = \frac{\rho - \rho_0 + \dfrac{z_0\epsilon}{k_BT}\left(\dfrac{\rho^2}{2} - \dfrac{\rho^3}{3}\right) - \dfrac{z_0\epsilon}{k_BT}\left(\dfrac{\rho_0^2}{2} - \dfrac{\rho_0^3}{3}\right)}{\rho_l - \rho_0 + \dfrac{z_0\epsilon}{k_BT}\left(\dfrac{\rho_l^2}{2} - \dfrac{\rho_l^3}{3}\right) - \dfrac{z_0\epsilon}{k_BT}\left(\dfrac{\rho_0^2}{2} - \dfrac{\rho_0^3}{3}\right)} \tag{37}$$

For $\rho_l = 0$, eq 37 can be simplified as

$$\frac{x}{l} = 1 - \frac{\rho + \dfrac{z_0\epsilon}{k_BT}\left(\dfrac{\rho^2}{2} - \dfrac{\rho^3}{3}\right)}{\rho_0 + \dfrac{z_0\epsilon}{k_BT}\left(\dfrac{\rho_0^2}{2} - \dfrac{\rho_0^3}{3}\right)} \tag{38}$$

   Figures 2−4 illustrate density distributions predicted by eq 38 for $\rho_0 = 0.8$ at supercritical, critical, and subcritical temperatures with various $z_0\epsilon/k_BT$. As shown by Figure 2, at a supercritical temperature, the density goes down smoothly from $\rho_0 = 0.8$ (at $x = 0$) to $\rho_l = 0$ (at $x = l$). Figure 3 indicates that, at the critical temperature, function 38 has a point with an infinite derivative.
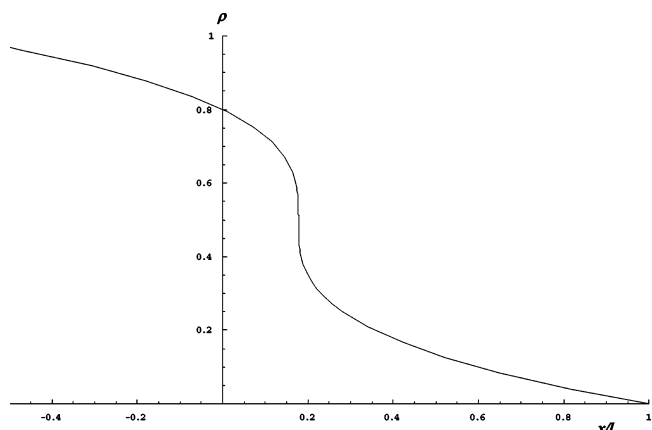

Figure 3. Density distribution for $\rho_0 = 0.8$, $\rho_l = 0$, and a critical temperature of $z_0\epsilon/k_BT = -4$.
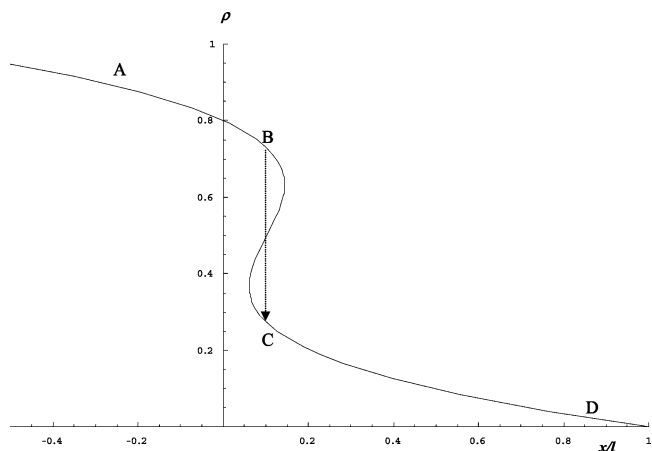

Figure 4. Density distribution for $\rho_0 = 0.8$, $\rho_l = 0$, and a subcritical temperature of $z_0\epsilon/k_BT = -4.3$.
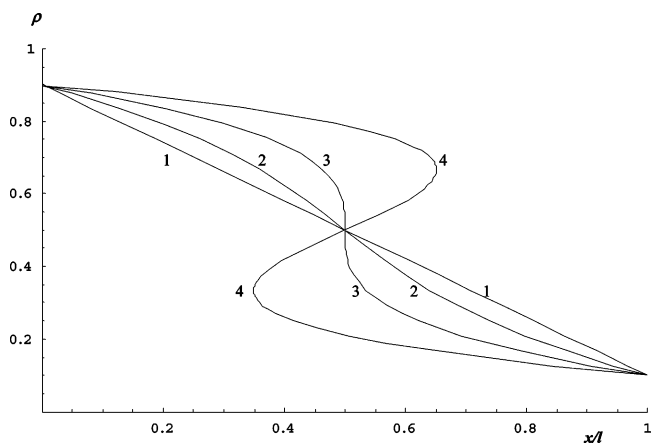

Figure 5. Density distribution at $\rho_0 = 0.1$, $\rho_l = 0.9$, and various $z_0\epsilon/k_BT$: 0 (1); −3 (2); −4 (3); −4.5 (4).

   Figure 4 shows function 38 at $\rho_0 = 0.8$ and $z_0\epsilon/k_BT = -4.3$ (a subcritical temperature). As shown by Figure 4, the point with an infinite derivative turns into a loop, indicating a phase transition; the step from point B to point C indicates a phase transition from a high density phase to a low density phase.
   Figures 2−4 show density distributions for asymmetric boundary conditions. Since the phase diagram for the mean-field approximation is symmetric, symmetric boundary conditions should result in density distributions symmetric with respect to $x/l = 0.5$ and $\rho = 0.5$. This is illustrated in Figure 5, showing density distributions predicted by eq 37 at $\rho_0 = 0.1$, $\rho_l = 0.9$, and various $z_0\epsilon/k_BT$.
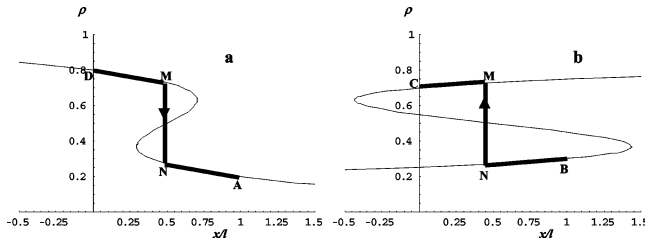
Figure 6. Density distribution predicted by eq 37 at $z_0\epsilon/k_BT = -4.3$ and boundary conditions from different parts of the phase diagram: (a) $\rho_0 = 0.8$ and $\rho_l = 0.2$; (b) $\rho_0 = 0.7$ and $\rho_l = 0.3$.

Figure 6 gives density distributions predicted by eq 37 at $z_0\epsilon/k_BT = -4.3$ and for boundary conditions from different parts of the phase diagram (shown in Figure 7). The boundary conditions in part a are in the one-phase regions at points A and D. For part b, the boundary conditions correspond to a supersaturated vapor (point B) and supersaturated liquid (point C). As shown by Figure 6, a small change of the density at the boundary conditions (from undersaturated to supersaturated) results in a dramatic change of the density distribution predicted by eq 37. For the undersaturated boundary conditions, in part a, the flux goes from point D (liquid) to point A (vapor) through points M and N with evaporation. For the supersaturated boundary conditions, in part b, the flux goes the opposite way, from point B (vapor) to point C (liquid) with condensation from N to M.

Deviations from Mean Field

As shown by the derivation of eq 21, the factor $\rho(1 - \rho)$ comes from a mean-field approximation in the calculation of fluxes in eqs 5–8. This factor comes from the probability of having a molecule on a certain site of the grid and having a neighboring site empty. The non-mean-field version of this probability, P_N, can be written as

$$P_N = \rho P_{in} \tag{39}$$

where P_{in} is the insertion probability. With this correction, eqs 21 and 22 can be generalized to the following non-mean-field form:

$$\frac{1}{D}\frac{\partial\rho}{\partial t} = \nabla^2\rho + \mathrm{div}(P_N\nabla H) \tag{40}$$

The term $\mathrm{div}(P_N\nabla H) = (\partial/\partial x)[P_N(\partial H/\partial x)] + (\partial/\partial y)[P_N(\partial H/\partial y)] + (\partial/\partial z)[P_N(\partial H/\partial z)]$ is due to interactions between particles and/or with an external field. Since $\nabla^2 = \mathrm{div}(\mathrm{grad})$, then eq 40 is equivalent to

$$\frac{1}{D}\frac{\partial\rho}{\partial t} = \mathrm{div}(\mathrm{grad}\,\rho + P_N\,\mathrm{grad}\,H) \tag{41}$$

Physically, P_N represents the density of molecule–vacancy pairs. They can be considered "pseudoparticles" which determine the diffusion.

Note that the mean-field factor, $\rho(1 - \rho)$, in eqs 21 and 22 represents entropy; however, the energy term, $H(\rho,x,y,z)$, in eqs 21 and 22 is written in a general form and does not have mean-field limitations. Equation 41 has both the energy term and the entropy term in a general (non-mean-field) form.

To illustrate the difference between eqs 21 and 41, consider the steady-state flux given by eq 26 and its generalized one-dimensional version from eq 41:

$$F_t = -D\left[\frac{\partial\rho}{\partial x} + \rho(1 - \rho)\frac{\partial H}{\partial x}\right] \tag{42}$$

$$F_t = -D\left[\frac{\partial\rho}{\partial x} + P_N\frac{\partial H}{\partial x}\right] \tag{43}$$

If $H = H(\rho)$ (no external field), then eqs 42 and 43 are

$$F_t = -D\frac{\partial\rho}{\partial x}\left[1 + \rho(1 - \rho)\frac{\partial H}{\partial\rho}\right] \tag{44}$$

$$F_t = -D\frac{\partial\rho}{\partial x}\left[1 + P_N\frac{\partial H}{\partial\rho}\right] \tag{45}$$

For mean-field $H(\rho)$ given by eq 30, eq 44 can be written as

$$F_t = -D\frac{\partial\rho}{\partial x}\left[1 + \rho(1 - \rho)\frac{z_0\epsilon}{k_BT}\right] \tag{46}$$

Therefore, the flux is the product of $-D(\partial\rho/\partial x)$ and the function

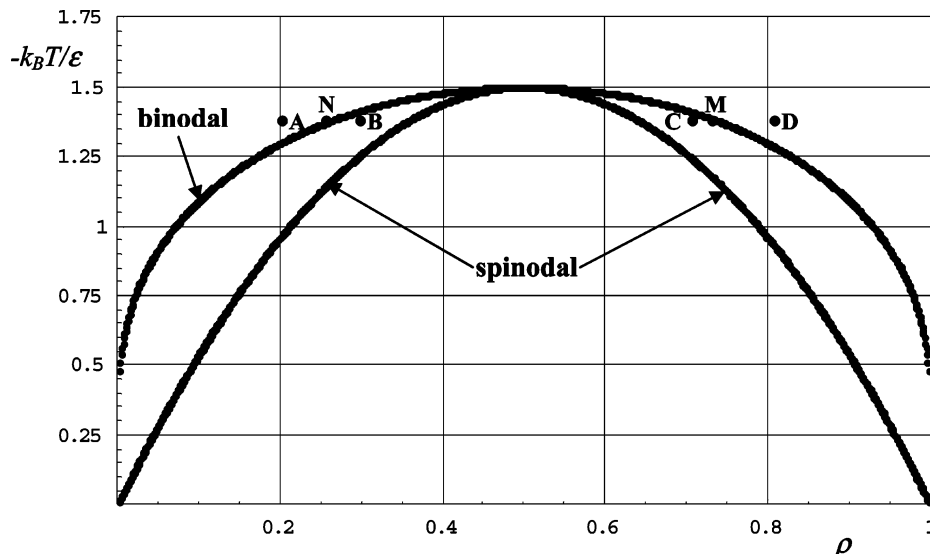**Figure 7.** Mean-field phase diagram.

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$$F_S = 1 + \rho(1 - \rho)\frac{z_0\epsilon}{k_B T} \qquad (47)$$

In the mean-field approximation, it is known that $F_S = 0$ defines the spinodal. Thus, the flux through the system is the product of the diffusion coefficient, the density gradient, and the spinodal function, F_S. Equation 47 gives the mean-field version of this function; however, comparison of eqs 44−46 indicates that this function can be written in a more general way:

$$F_S = 1 + P_N\frac{\partial H}{\partial \rho} \qquad (48)$$

If the entropy term is mean-field and the energy term is exact (as in eq 44 where H is not specified), then

$$F_S = 1 + \rho(1 - \rho)\frac{\partial H}{\partial \rho} \qquad (49)$$

In all cases,

$$F_t = -DF_S\frac{\partial \rho}{\partial x} \qquad (50)$$

Note that, in the diffusion literature,[7] the coefficient of proportionality between F_t and $-\partial\rho/\partial x$ is considered as a generalized (density dependent) coefficient of diffusion, D^*. As seen from eq 50, $D^* = DF_S$; at the spinodal where $F_S = 0$, D^* vanishes. This result has experimental confirmation: D^* near critical or consolute points goes to zero. In particular, this has been observed for diffusion in binary systems including triethylamine−water, isobutyric acid−water, hexane−nitrobenzene, analine−cyclohexane, and carbon tetrachloride−perfluoromethylcyclohexane.[7] Similar results are known for diffusion in systems with surfactants at the critical micelle concentration (cmc), such as cetyltrimethylammonium bromide adsorbed to the silica−aqueous interface,[27] and diffusion mechanisms dramatically change if a system containing surfactant (such as hexadecylpyridinium chloride[28]) passes through the cmc.

Equation 50 has another interesting implication for equilibrium (without an external field) where

$$F_t = -DF_S\frac{\partial \rho}{\partial x} = 0 \qquad (51)$$

If $F_S \neq 0$, the vanishing of $(\partial\rho/\partial x)F_S$ in eq 51 only can be due to $\partial\rho/\partial x = 0$. Therefore, far from boundaries (to avoid external fields), $\rho(x) = $ constant. However, if $F_S = 0$, equality 51 can be satisfied at equilibrium without $\rho(x) = $ constant. At $F_S = 0$, fluctuations of density become macroscopic and $\rho(x)$ can be an arbitrary function.

External Field

In the presence of an external field, H depends explicitly not only on ρ but also on position and coordinates. This can happen, for example, where a fluid is in contact with a solid surface and the field from the surface results in adsorption. Consider eq 23 where $H = H(\rho,x)$ and $C_1 = 0$ (equilibrium). In this case, eq 23 can be written as

$$\frac{d\rho}{\rho(1 - \rho)} = -dH \qquad (52)$$

After integration from ρ to ρ_∞, eq 52 gives

$$\ln\frac{\rho(1 - \rho_\infty)}{(1 - \rho)\rho_\infty} + H - H_\infty = 0 \qquad (53)$$

which is the well-known Ono−Kondo equation for adsorption.[23,29,30]

If H is an explicit function of x only, $H = H(x)$, then eq 23 is

$$\frac{\partial \rho}{\partial x} + H'(x)\rho(1 - \rho) = C_1 \qquad (54)$$

where $H'(x) = \partial H/\partial x$. If $H(x)$ is a linear function of x, then $H'(x) = $ constant $= \lambda$ and general solution of eq 54 can be represented as

$$x + C_2 = \int\frac{d\rho}{C_1 - \lambda\rho(1 - \rho)} \qquad (55)$$

where C_1 and C_2 are arbitrary constants to be determined from the boundary conditions.

For $\rho \ll 1$ and for $H = H(x,y,z)$ (depending only on coordinates and not on ρ), eq 22 turns into the well-known Fokker−Planck equation for diffusion with drift:[18−20]

$$\frac{1}{D}\frac{\partial \rho}{\partial t} = \frac{\partial^2\rho}{\partial x^2} + \frac{\partial^2\rho}{\partial y^2} + \frac{\partial^2\rho}{\partial z^2} + \frac{\partial}{\partial x}(\rho H'_x) + \frac{\partial}{\partial y}(\rho H'_y) + \frac{\partial}{\partial z}(\rho H'_z) \qquad (56)$$

where $H'_x = \partial H(x,y,z)/\partial x$, $H'_y = \partial H(x,y,z)/\partial y$, and $H'_z = \partial H(x,y,z)/\partial z$.

Generally, H is a function of density and coordinates. In particular, for diffusion in a condensed medium or for systems with chemical bonding, the energy profile can be viewed in terms of transition-state theory (TST).[31] In this case, the maximum in energy profile d in Figure 1 is a transition state (transition from point i − 1 to point i + 1 with a potential barrier at point i). In the spirit of TST, eq 18 can be represented in the following form:

$$\frac{1}{D}\frac{\partial \rho_i}{\partial t} \approx \frac{K}{z_0}P_{Ni}\left\{\frac{1 - \rho_{i+1}}{1 - \rho_i}[\exp(F_{i+1} - F_i) - 1] + \frac{1 - \rho_{i-1}}{1 - \rho_i}[\exp(F_{i-1} - F_i) - 1]\right\} \qquad (57)$$

Here, $P_{Ni} = \rho_i(1 - \rho_i)$, $F_i = H_i - TS_i$, and $F_{i\pm1} = H_{i\pm1} - TS_{i\pm1}$, where $S_i = -(1/k_B T)k_B \ln[\rho_i/(1 - \rho_i)] = -(1/T)\ln[\rho_i/(1 - \rho_i)]$ and $S_{i\pm1} = -(1/T)\ln[\rho_{i\pm1}/(1 - \rho_{i\pm1})]$ (normalized configurational entropy). In eq 57, the terms $\exp(F_{i\pm1} - F_i)$ reflect surmounting free energy barriers and the factors $(1 - \rho_{i\pm1})/(1 - \rho_i)$ are entropic corrections to the barriers due to changes in the geometry of free space. At $\rho_i \ll 1$ and $\rho_{i\pm1} \ll 1$, eq 57 can be rewritten as

$$\frac{1}{D}\frac{\partial \rho_i}{\partial t} \approx \frac{K}{z_0}P_{Ni}[\exp(F_{i+1} - F_i) + \exp(F_{i-1} - F_i) - 2] \qquad (57a)$$

and diffusion is determined by free energy barriers as assumed in TST.

Driving Forces of Diffusion

It is reasonable to assume that the diffusion flux is directly proportional to a gradient of some (driving) force. Then, eq 43 can be written in the following form:

$$F_t = -D\frac{\partial Y}{\partial x} \qquad (58)$$

where

$$\frac{\partial Y}{\partial x} = \frac{\partial \rho}{\partial x} + P_N\frac{\partial H}{\partial x} \qquad (59)$$

Equation 59 gives

$$dY = d\rho + P_N\,dH \qquad (60)$$

or

$$Y = \rho + \int P_N\,dH \qquad (61)$$

As seen from eq 61, the driving force of diffusion has two components: the first, ρ, is "ideal" or classical; the second, $\int P_N\,dH$, reflects the influence of interactions on the diffusion flux. In this second term, the density of molecule−vacancy pairs (pseudoparticles), P_N, is a key variable. This is in agreement with diffusion mechanisms of gelation, glassification, and jamming[32] in dense molecular systems where "the geometry of empty space is the key"[33] to dynamics and phase transitions. For these systems, the authors of ref 33 proposed a new order parameter, "dynamically available volume (unoccupied space that is available to the motion of particles)" which is an analogue of P_N.

As shown by equation 59, the gradient of potential energy multiplied by P_N gives the contribution to the flux due to interactions. In condensed regions of diffusant (such as clusters), P_N is small, and in gaseous regions, $\partial H/\partial x$ is small. However, at the surfaces of clusters, both terms are significant, and the term $P_N\,dH$ in eq 60 represents a change in potential energy at such surfaces. This indicates a consistency with the GLM model[16] using the Cahn−Hilliard approach and the Ginzburg−Landau free energy functional with classical, ρ, and surface, $A(\nabla\rho)^2$, components.

Generalization for Density Dependent D

Equations 21 and 41 are written for a case where the diffusion coefficient is constant (not depending on ρ). If $D = D(\rho)$, the mass balance equation can be represented more generally as $\partial\rho/\partial t = -\text{div}\,\vec{F}_t$,[34] where $\vec{F}_t$ is the flux vector. Then, eqs 21 and 41 can be rewritten as

$$\frac{\partial\rho}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial\rho}{\partial x}\right) + \frac{\partial}{\partial x}\left[D\rho(1-\rho)\frac{\partial H}{\partial x}\right] \qquad (62)$$

$$\frac{\partial\rho}{\partial t} = \text{div}[D(\text{grad}\,\rho + P_N\,\text{grad}\,H)] \qquad (63)$$

respectively.

It can be useful to have flux in the form of eq 58

$$F_t = -D_0\frac{\partial Y^*}{\partial x} \qquad (64)$$

where D_0 is a density independent constant and Y^* is a "true" driving force. Since eqs 64 and 58 have to be equivalent,

$$D_0\frac{\partial Y^*}{\partial x} = D(\rho)\frac{\partial Y}{\partial x} \qquad (65)$$

which gives

$$D_0\,dY^* = D(\rho)\,dY \qquad (66)$$

and

$$Y^* = \frac{1}{D_0}\int D(\rho)\,dY \qquad (67)$$

Combining eqs 60 and 67 results in

$$Y^* = \int \tilde{D}\,d\rho + \int \tilde{D}P_N\,dH \qquad (68)$$

where $\tilde{D} = D(\rho)/D_0$. Note that, for non-interacting particles, $\int \tilde{D}P_N\,dH = 0$ and the flux is determined by the gradient of $\int \tilde{D}\,d\rho$ which turns into ρ at $D(\rho) = $ constant.

Conclusion

A correction to the partial differential equation of diffusion is derived using density functionals for fluxes and the Metropolis algorithm in the mass balance equation. The result is consistent with the theory of Giacomin, Lebowitz, and Marra[15−17] in the hydrodynamic limit. The new equation can have multiple solutions, reflecting density distributions of coexisting and metastable phases.

It is shown that the diffusion of interacting molecules is driven by two variables: the density gradient of molecules and the density of molecule−vacancy pairs (pseudoparticles).

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