Numerical treatment of the dynamics of a conserved order parameter in the presence of walls

Jun-ichi Fukuda,[1,2,*] Makoto Yoneya,[1,2] and Hiroshi Yokoyama[1,2]

[1]*Nanotechnology Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), 1-1-1 Umezono, Tsukuba 305-8568, Japan*

[2]*Liquid Crystal Nano-System Project, ERATO/SORST, Japan Science and Technology Agency, 5-9-9 Tokodai, Tsukuba 300-2635, Japan*

We discuss how the diffusive dynamics of a conserved order parameter should be numerically treated when impenetrable wall surfaces are present and interact with the degrees of freedom characterized by the order parameter. We derive the discretization scheme for the dynamics, paying particular attention to the conservation of the order parameter in the strict numerical sense. The discretized chemical potential, or the functional derivative of the free energy, contains a surface contribution inversely proportional to the grid spacing Δz, which was proposed heuristically in a recent paper of Henderson and Clarke [Macromol. Theory Simul. **14**, 435 (2005)]. Although apparently that surface contribution diverges in the continuum limit $\Delta z \to 0$, we can show, by an analytic argument and numerical calculations, that this divergence does not yield any anomalies, and that our discretization scheme is well defined in this limit. We also discuss the correspondence of our treatment to the model proposed by Puri and Binder [Phys. Rev. A **46**, R4487 (1992)] extensively used for the present problem.

I. INTRODUCTION

How a liquid in a vapor, or a mixture of liquids, behaves at and in the vicinity of solid surfaces has long been a substantial problem in fundamental science as well as in practical applications. A typical and important example is wetting phenomena [1–5]. One of the pioneering studies using a continuum theory is due to Cahn [6], who discussed the wetting of a two-phase fluid close to its critical point. His theory is based on the free energy as a functional of a scalar order parameter ψ characterizing the fluid composition. The free energy is composed of the bulk part of the Landau-Ginzburg type and the surface part depending only on the surface composition field. It is then formally written as

$$\frac{F[\psi]}{k_B T} = \int_{\Omega} d^d r \left\{ f_{\mathrm{b}}[\psi(\mathbf{r})] + \frac{1}{2} \kappa (\nabla \psi)^2 \right\} + \int_{\partial\Omega} d^{d-1} r f_{\mathrm{s}}[\psi(\mathbf{r})], \tag{1}$$

where Ω is the volume of the system, d is the spatial dimension, f_{b} is the local free energy density in the bulk, and the excess of the free energy due to inhomogeneity is taken into account in the second term. The last term is associated with the short-range interaction between the fluid and the substrate surface $\partial\Omega$. Numerous theoretical studies [7] extending the Cahn's approach have been done concerning the static nature of wetting phenomena.

Dynamical aspects of wetting phenomena have also been of fundamental interest. Over the last decade, considerable attention has been paid to the phase separation dynamics of a binary mixture in the presence of a solid surface wetted preferably by one of the two components [8–16] as an important problem concerning dynamical wetting phenomena. To deal with that problem, appropriate equations governing the dynamics of the order parameter ψ at the surface as well as in the bulk must be given. When the hydrodynamic flow is not taken into account, the diffusive dynamics of ψ in the bulk is readily written, with the assumption of Fick's law and the appropriate mobility M, as

$$\frac{\partial}{\partial t} \psi = \nabla \cdot \left(M \nabla \frac{\delta F / k_B T}{\delta \psi} \right). \tag{2}$$

Equation (2), with an appropriate bulk free energy, is often referred to as model *B* following the nomenclature of Hohenberg and Halperin [17]. When ψ characterizes the fluid composition as mentioned above, it must be treated as a conserved quantity. The conservation of ψ is properly taken into account in the model *B* equation (2).

How the order parameter ψ evolves at the surface is, however, not trivial. From Eq. (1), the surface chemical potential reads $df_s / d\psi + \boldsymbol{\nu} \cdot \kappa \nabla \psi$, where $\boldsymbol{\nu}$ is a unit vector normal to $\partial\Omega$ and pointing outwards. Therefore a possible candidate for the dynamics of ψ at the surface is

$$\frac{\partial}{\partial t} \psi = M_{\mathrm{s}} \left(\frac{df_s}{d\psi} + \boldsymbol{\nu} \cdot \kappa \nabla \psi \right), \tag{3}$$

which is indeed employed by Jacqmin [18], who discussed the dynamics of a moving contact line. There is, however, no guiding principle of determining the "surface mobility" M_{s} in the model equation (3) and therefore Eq. (3) is just an assumption.

One of the pioneering theoretical studies concerning how a surface affects the dynamics of a system with a conserved order parameter was done by Binder and Frisch [19]. Starting from the Kawasaki spin-exchange model [20], they derived discrete and continuum versions of the equations of motion for the conserved spin variable in the presence of a wall. Their equations of motion contain only one character-

*Electronic address: fukuda.jun-ichi@aist.go.jp

istic time, which is associated with the spin-exchange probability. Therefore in one of their model equations corresponding to Eq. (3), the surface mobility is automatically determined by this spin-exchange characteristic time. Using the continuum version of the Binder-Frisch model, and explicitly taking into account the boundary condition concerning the impenetrability of the wall, Puri and Binder [21] carried out extensive numerical calculations to investigate the surface enrichment or the effect of the presence of surfaces on the dynamics of the phase separation of binary mixtures. They showed the growth of composition fluctuations in the vicinity of a surface, which well reproduced corresponding experiments. Their model (which we will refer to as the PB model) and its extensions, consisting of the dynamic equation in the bulk (2), the surface diffusion equation (3), and the requirement of no order-parameter flux through the surface, have been extensively used in subsequent numerical studies concerning the effect of an impenetrable surface on the dynamics of a fluid in its vicinity [22–28].

However, due to the possible numerical errors in the discretization of the model and the nonconserved form of the surface diffusion equation (3), it is not trivial what kind of discretization guarantees the overall conservation of ψ in the strict numerical sense. Moreover, the condition of no order-parameter flux involves third-order spatial derivative at the surface [see Eq. (36) below], which requires the values of ψ on at least four grid points along the surface normal. Therefore care must be taken of the time evolution of those four grid points (or grid layers in two or more dimensions). Nevertheless, to our knowledge, none of the previous work using the PB model presented in detail how it was discretized.

Moreover, Henderson and Clarke [29] (we will abbreviate them as HC) recently demonstrated that the PB model gives inconsistent results when the grid spacing is varied. They also proposed a model different from the PB model; instead of using a separate equation (3) for the dynamics of ψ at the surface, they just applied Eq. (2) to the surface as well as to the bulk. Furthermore, their surprising claim is that in the treatment of the surface, the numerical grid spacing must be included in the dynamical equation explicitly, although the grid spacing does not have any physical meaning of its own. Their numerical results, therefore, cast a fundamental doubt to the validity and the consistency of the PB model. However, the argument of Henderson and Clarke on their model lacks a mathematical justification; their justification of the model relies only on the consistency of its numerical results.

Given those ambiguities in the previous numerical treatments of the dynamics of a conserved order parameter in the presence of a wall surface, it should be worthwhile to discuss thoroughly how the equation of motion for a conserved order parameter should be discretized when a wall is present, which is the aim of this paper. Together with an appropriate discretization of the free energy (1) and the equation of motion for the order parameter ψ in the bulk (2), we derive the equation for the dynamics of ψ at the wall surfaces, paying particular attention to the overall conservation of ψ in the strict numerical sense. Our equations are similar to those of the HC model [29], in that the grid spacing appears explicitly in the equations. We show by an analytical argument together with numerical test calculations that this apparent depen-

dence of the model equation on the grid spacing does not play any harmful role, that is, our model is consistent when the grid spacing is varied. Our results clearly demonstrate that naive discretization of Eq. (3) does not make sense, insofar as one wants to start with the free energy of the form of Eq. (1). We also discuss how the PB model, which does not explicitly contain the numerical grid spacing, is related with ours.

This paper is organized as follows. Section II gives our numerical treatment of the dynamics of a conserved order parameter in the presence of walls. In Sec. III A, we show analytically and by numerical test calculations that our model presented in Sec. II is consistent when the grid spacing is varied. We discuss in Sec. III B the similarities and differences between our model and the previous corresponding models, the PB model, and the HC model. Section IV concludes this paper.

II. NUMERICAL TREATMENT

We consider a one-dimensional semi-infinite system where a planar impenetrable wall is located at $z=0$ and the z axis is parallel to the wall normal. We restrict ourselves to one dimension just for the simplicity and clarity of the presentation, and extension to higher dimensions is straightforward.

We introduce a conserved order parameter $\psi(z,t)$ describing the state of the system. The conservation of ψ implies

$$\int_0^\infty dz\,\psi(z,t) = \int_0^\infty dz\,\psi(z,0), \tag{4}$$

or equivalently

$$\frac{\partial}{\partial t}\int_0^\infty dz\,\psi(z,t) = 0 \tag{5}$$

throughout the time evolution ($t>0$). The free energy (1) in our one-dimensional system per area is written as

$$\frac{F_{\text{tot}}[\psi(z)]}{k_B T} = \frac{F[\psi(z)]}{k_B T} - \mu \int_0^\infty dz\,\psi(z), \tag{6}$$

with

$$\frac{F[\psi(z)]}{k_B T} = \int_0^\infty dz\left[f_{\text{b}}(\psi(z)) + \frac{1}{2}\kappa\left(\frac{\partial}{\partial z}\psi(z)\right)^2\right] + f_{\text{s}}(\psi(0)). \tag{7}$$

Here we have introduced a Lagrange multiplier μ ensuring the conservation of the order parameter ψ, Eq. (4). Hereafter in this section we choose the unit of the energy such that $k_B T=1$. We note that the equilibrium profile of $\psi(z)$ is determined by $\delta F_{\text{tot}}/\delta\psi(z)=0$, i.e.

$$\frac{\delta F}{\delta\psi(z)} = \mu, \tag{8}$$

together with the constraint (4).

The time evolution of the order parameter in the bulk ($z>0$) is written formally in terms of a flux $j(z,t)$ of the order parameter as

$$\frac{\partial}{\partial t}\psi(z,t) = -\frac{\partial}{\partial z}j(z,t). \tag{9}$$

Equation (9) is a differential description of the conservation of ψ. We assume Fick's law for $j(z)$

$$j(z) = -M\frac{\partial}{\partial z}\frac{\delta F}{\delta\psi(z)}. \tag{10}$$

In principle, the mobility M can be a function of ψ, the position z, and the time t, but such dependence is not essential in the following discussion. Notice also that $j(z)=0$ [or $\partial(\delta F/\delta\psi(z))/\partial z=0$] that must be fulfilled in equilibrium can be regarded as a differential form of Eq. (8), the equilibrium condition. In the case of constant M, Eqs. (9) and (10) reduce to

$$\frac{\partial}{\partial t}\psi = M\frac{\partial^2}{\partial z^2}\frac{\delta F}{\delta\psi}, \tag{11}$$

which is the one-dimensional version of model B [see Eq. (2)].

We note that the time evolution of the order parameter at the wall $\psi(0)$ is not a trivial matter from the argument above, because the functional derivative of Eq. (7) reads

$$\frac{\delta F}{\delta\psi(z)} = f_{\rm b}'(\psi(z)) - \kappa\frac{\partial^2\psi(z)}{\partial z^2} + \left(-\kappa\frac{\partial\psi(z)}{\partial z} + f_{\rm s}'(\psi(z))\right)\delta(z), \tag{12}$$

which contains a δ function. Here $f_{\rm b/s}'(\psi) \equiv df_{\rm b/s}/d\psi$. In the PB model, the time evolution of $\psi(0)$ is essentially driven by the surface chemical potential, which in the notation of the present model, is written as $-\kappa\frac{\partial\psi}{\partial z}|_{z=0} + f_{\rm s}'(\psi(0))$. The PB model also includes a second boundary condition ensuring the conservation of ψ, that is, $j(0)=0$. We emphasize that the PB model originates not from a continuum theory, but from a lattice model and taking its continuum limit [19]. That is the reason why they did not consider explicitly how the δ function should be treated. The details of the PB model in connection with ours will be discussed below in Sec. III B 1.

Now we discretize the system with the spacing Δz, and define $\psi_i = \psi(i\Delta z)$. A natural discretization of the free energy (6) reads

$$F_{\rm tot}[\{\psi_i\}] = F[\{\psi_i\}] - \mu\sum_{i=0}^{\infty}\left(\frac{\psi_i+\psi_{i+1}}{2}\right)\Delta z, \tag{13}$$

with

$$F[\{\psi_i\}] = \sum_{i=0}^{\infty}\left\{\frac{f_{\rm b}(\psi_i)+f_{\rm b}(\psi_{i+1})}{2} + \frac{1}{2}\kappa\left(\frac{\psi_{i+1}-\psi_i}{\Delta z}\right)^2\right\}\Delta z$$
$$+ f_{\rm s}(\psi_0). \tag{14}$$

Here we have employed a simple trapezoidal formula [30] for the evaluation of the integral. The functional derivative $\delta F/\delta\psi(z)$ in the continuum description is replaced by a partial differentiation of the discretized F with respect to ψ_i

$$\frac{1}{\Delta z}\frac{\partial F}{\partial\psi_i} = \frac{1}{\Delta z}\frac{\partial F_{\rm tot}}{\partial\psi_i} + \mu = f_{\rm b}'(\psi_i) - \kappa\frac{\psi_{i-1}-2\psi_i+\psi_{i+1}}{(\Delta z)^2} \quad (i\geq 1), \tag{15}$$

$$\frac{2}{\Delta z}\frac{\partial F}{\partial\psi_0} = \frac{2}{\Delta z}\frac{\partial F_{\rm tot}}{\partial\psi_0} + \mu = f_{\rm b}'(\psi_0) + \left\{-\kappa\frac{\psi_1-\psi_0}{\Delta z} + f_{\rm s}'(\psi_0)\right\}\frac{2}{\Delta z}$$
$$= f_{\rm b}'(\psi_0) - \kappa\frac{\psi_0-2\psi_1+\psi_2}{(\Delta z)^2} + \left\{-\kappa\frac{-3\psi_0+4\psi_1-\psi_2}{2\Delta z}\right.$$
$$\left.+ f_{\rm s}'(\psi_0)\right\}\frac{2}{\Delta z}. \tag{16}$$

We notice that $(\psi_{i-1}-2\psi_i+\psi_{i+1})/(\Delta z)^2 = (\partial^2\psi/\partial z^2)|_{z=i\Delta z} + \mathcal{O}((\Delta z)^2)$, $(-3\psi_0+4\psi_1-\psi_2)/(2\Delta z) = (\partial\psi/\partial z)|_{z=0} + \mathcal{O}((\Delta z)^2)$, and $(\psi_0-2\psi_1+\psi_2)/(\Delta z)^2 = (\partial^2\psi/\partial z^2)|_{z=0} + \mathcal{O}(\Delta z)$. Therefore, if we regard $(2/\Delta z)\delta_{i,0}$ as the discretized version of the δ function $\delta(z)$, Eqs. (15) and (16) can be considered to represent in a well-defined manner the functional derivative (12) in the discretized space [31].

Our next step is to discretize the equation of motion for ψ, Eq. (9), together with the flux (10). We define the discretized flux as

$$j\left(\left(i+\frac{1}{2}\right)\Delta z\right) \equiv j_{i+1/2} = -M\frac{1}{\Delta z}\left(\frac{1}{\Delta z}\frac{\partial F}{\partial\psi_{i+1}} - \frac{1}{\Delta z}\frac{\partial F}{\partial\psi_i}\right) \tag{17}$$

for $i\geq 1$. The equation motion for ψ in the discretized space reads

$$\frac{\partial}{\partial t}\psi_i = -\frac{1}{\Delta z}(j_{i+1/2} - j_{i-1/2}). \tag{18}$$

How to discretize the time derivative is not important in the present discussion. We notice that for $i\geq 2$, Eqs. (17) and (18) yield a well-defined discretization of model B equation (11).

To find out how ψ_0 and ψ_1 should evolve with time in the discretized space, we recall Eq. (5) that implies the conservation of ψ. The discretized version of Eq. (5) is

$$0 = \frac{\partial}{\partial t}\sum_{i=0}^{\infty}\frac{\psi_i+\psi_{i+1}}{2}\Delta z = \Delta z\left\{\frac{1}{2}\frac{\partial}{\partial t}\psi_0 + \sum_{i=1}^{\infty}\frac{\partial}{\partial t}\psi_i\right\}, \tag{19}$$

where we have again used the trapezoidal formula for the discretization of the integral. From Eqs. (18) and (19), we find

$$\frac{\partial}{\partial t}\psi_0 = -\frac{2}{\Delta z}j_{1/2}, \tag{20}$$

where $j_{1/2}$ is yet to be determined. We note that when we define an artificial flux at $z=-\frac{1}{2}\Delta z$ as $j_{-1/2}=-j_{1/2}$, Eq. (20) reduces to Eq. (18). Moreover, the flux at $z=0$ then reads $j(z=0) = \frac{1}{2}(j_{1/2}+j_{-1/2}) + \mathcal{O}((\Delta z)^2) = \mathcal{O}((\Delta z)^2)$, which is another manifestation of the impenetrability of the wall at $z=0$, although it is realized in the strict sense in Eq. (19).

Care must be taken when we define $j_{1/2}$. In equilibrium, $j_{1/2}=0$ must be satisfied. From Eqs. (15) and (16), the equi-

librium conditions at $i=0$ and $i=1$ read $\mu=(1/\Delta z)(\partial F/\partial \psi_1)$ $=(2/\Delta z)(\partial F/\partial \psi_0)$. Then the appropriate definition of $j_{1/2}$ should be

$$j_{1/2} = -M \frac{1}{\Delta z} \left(\frac{1}{\Delta z} \frac{\partial F}{\partial \psi_1} - \frac{2}{\Delta z} \frac{\partial F}{\partial \psi_0} \right). \qquad (21)$$

Now that $j_{1/2}$ is given, the time evolution of ψ_0 and ψ_1 is also well defined. Finally we can adopt any numerically feasible discretization scheme for the discretization of the time derivative, including explicit Euler, fully implicit, and Crank-Nicholson schemes [30].

To summarize, our numerical scheme of the dynamics of a conserved order parameter ψ is implemented by Eq. (18), together with an appropriate discretization for $\partial/\partial t$ and $j_{-1/2}=-j_{1/2}$. The discretized flux j is given by Eqs. (17) and (21), with the discretized free energy (14). When we define

$$\left. \frac{\delta F_b}{\delta \psi} \right|_i = \begin{cases} f_b'(\psi_i) - \kappa \dfrac{\psi_{i-1} - 2\psi_i + \psi_{i+1}}{(\Delta z)^2} & (i \geq 1) \\ f_b'(\psi_0) - \kappa \dfrac{\psi_0 - 2\psi_1 + \psi_2}{(\Delta z)^2} & (i=0), \end{cases} \qquad (22)$$

the equations for the time evolution of ψ_i can be explicitly written as

$$\frac{\partial}{\partial t}\psi_i = M \frac{1}{(\Delta z)^2} \left(\left. \frac{\delta F_b}{\delta \psi} \right|_{i-1} - 2 \left. \frac{\delta F_b}{\delta \psi} \right|_i + \left. \frac{\delta F_b}{\delta \psi} \right|_{i+1} \right) \quad (i \geq 2), \qquad (23)$$

$$\frac{\partial}{\partial t}\psi_1 = M \frac{1}{(\Delta z)^2} \left(\left. \frac{\delta F_b}{\delta \psi} \right|_0 - 2 \left. \frac{\delta F_b}{\delta \psi} \right|_1 + \left. \frac{\delta F_b}{\delta \psi} \right|_2 \right. $$
$$\left. + \left\{ -\kappa \frac{-3\psi_0 + 4\psi_1 - \psi_2}{2\Delta z} + f_s'(\psi_0) \right\} \frac{2}{\Delta z} \right), \quad (24)$$

$$\frac{\partial}{\partial t}\psi_0 = M \frac{1}{(\Delta z)^2} \left(\left. \frac{\delta F_b}{\delta \psi} \right|_{-1} - 2 \left. \frac{\delta F_b}{\delta \psi} \right|_0 + \left. \frac{\delta F_b}{\delta \psi} \right|_1 \right. $$
$$\left. - 2 \left\{ -\kappa \frac{-3\psi_0 + 4\psi_1 - \psi_2}{2\Delta z} + f_s'(\psi_0) \right\} \frac{2}{\Delta z} \right). \quad (25)$$

As noted above, Eq. (23) is just the discretization of the model B equation (11) in the bulk. In Eq. (25), we have defined $\left. \frac{\delta F_b}{\delta \psi} \right|_{-1} = \left. \frac{\delta F_b}{\delta \psi} \right|_1$, which is consistent with the definition of the flux $j_{-1/2}=-j_{1/2}$.

III. DISCUSSION

A. Consistency of our scheme with the variation of Δz

1. Analytical argument

One may wonder whether Eqs. (24) and (25) behave in a consistent and well-defined manner with the variation of Δz and in the limit $\Delta z \to 0$, because the surface contribution in Eqs. (24) and (25) apparently contains a factor $2/\Delta z$. To answer this question, we introduce a Fourier transform of $\psi_i = \psi(i\Delta z)$

$$\psi(q) = \Delta z \left\{ \frac{1}{2}\psi_0 + \sum_{i=1}^{\infty} \psi_i \cos(qi\Delta z) \right\}. \qquad (26)$$

Inverse Fourier transform of Eq. (26) is

$$\psi_i = \frac{2}{\pi} \int_0^{\pi/\Delta z} dq \, \psi(q) \cos(qi\Delta z). \qquad (27)$$

We note again that ψ_i implies $\psi(i\Delta z)$; therefore the spatial position indicated by i is different with the variation of Δz. Moreover, in the limit $\Delta z \to 0$, Eq. (26) becomes $\psi(q) = \int_0^{\infty} dz \psi(z) \cos(qz)$, with $z=i\Delta z$, which clearly implies that Eq. (26) is well defined in this limit. We also notice that $\psi(q)$ is insensitive to the variation of Δz as long as $q\Delta z \ll 1$.

From Eqs. (23)–(26), we can write down the equation for the time evolution of $\psi(q)$. A straightforward calculation yields

$$\frac{1}{M} \frac{\partial}{\partial t}\psi(q) = -\frac{2}{(\Delta z)^2}(1 - \cos(q\Delta z))\Delta z \left\{ \frac{1}{2}f_b'(\psi_0) \right. $$
$$\left. + \sum_{i=1}^{\infty} f_b'(\psi_i)\cos(qi\Delta z) \right\} - \frac{2\kappa}{(\Delta z)^4}(3 - 4\cos(q\Delta z) $$
$$+ \cos(2q\Delta z))\psi(q) - \frac{2}{(\Delta z)^2}(1 - \cos(q\Delta z))f_s'(\psi_0) \qquad (28)$$

The first line involves the Fourier transform of $f_b'(\psi_i)$, which we will denote by $f_b'(q)$. Equation (28) can be rewritten as

$$\frac{1}{M} \frac{\partial}{\partial t}\psi(q) = -q^2 f_b'(q) - \kappa q^4 \psi(q) - q^2 f_s'(\psi_0) + \mathcal{O}((\Delta z)^2). \qquad (29)$$

Since all the terms involved in Eq. (29) are well behaved in the limit $\Delta z \to 0$, Eq. (28), or equivalently Eq. (29), is well defined in this limit. Therefore we have shown that the apparent factor $2/\Delta z$ in Eqs. (24) and (25) yields no anomaly in the time evolution of ψ.

2. Numerical test

We also perform numerical test calculations to demonstrate in a clearer fashion the consistency of our scheme when Δz is varied. So long as the grid spacing Δz is spatially uniform, an infinite system cannot be dealt with numerically. Therefore in this section we consider a finite space $0 \leq z \leq L$ and incorporate a surface energy also at $z=L$. This is achieved just by adding $f_s(\psi(L))$ to the free energy, Eqs. (7) or (14). In general the functional form of the surface free energies at $z=0$ and at $z=L$ can be different. Here we choose the same form just for simplicity.

We adopt a quadratic form for the bulk and the surface free energies: $f_b(\psi) = \frac{1}{2}a\psi^2$ with $a=1$, and $f_s(\psi) = \frac{1}{2}b(\psi - \psi_{s0})^2$ with $b=2.5$ and $\psi_{s0}=0.5$. We choose $\kappa=1$ and $L=10$. By rescaling time t, we can set $M=1$. As the initial condition, we set $\psi_i(t=0)=\psi_{init}=0.1$ for any i. We note that the equilibrium profile of ψ for the present problem can be

TABLE I. The grid spacing Δz and the time increment Δt used in our numerical calculations.

Δz	Δt
0.25	2×10^{-4}
0.2	1×10^{-4}
0.1	1×10^{-5}
0.05	5×10^{-7}
0.02	1×10^{-8}

obtained analytically, which is given in the Appendix.

As the discretization of the time derivative, we employ a simple explicit Euler scheme, with the time increment Δt. The second term in the right-hand side of Eq. (28) plays a dominant role in the numerical stability of the present scheme. From the von Neumann analysis [30] of Eq. (28), we find that at least

$$8\kappa\Delta t \leq (\Delta z)^4 \qquad (30)$$

must be satisfied (notice that this is not a sufficient condition for the numerical stability). The grid spacing Δz and the time increment Δt used in our calculations are summarized in Table I.

Figure 1 shows the time evolution of the profile of ψ with $\Delta z = 0.25$. Since the system is symmetric about the center $z = 5$, only half of the system, i.e., $0 \leq z \leq 5$, is presented. At the initial stage, surface enrichment occurs because $\psi_{s0} > \psi(t=0)$. The surface enrichment is compensated by the decrease of ψ near the surface due to conservation. The depleted region moves and extends towards the center of the system, until equilibrium is reached.

To see the effect of the variation of the grid spacing Δz, we show in Fig. 2 the profiles of ψ for different Δz's at several given t's. We emphasize that in the case of $\Delta z = 0.25$ in Fig. 2(a), $t = 0.001$, only five iterations have been carried out and only nine grid points are present in the figure. Thus we can say that those profiles in Fig. 2(a) fall astonishingly well on one master curve, although the numerical resolution $\Delta z = 0.25$ is not at all sufficient enough to describe the
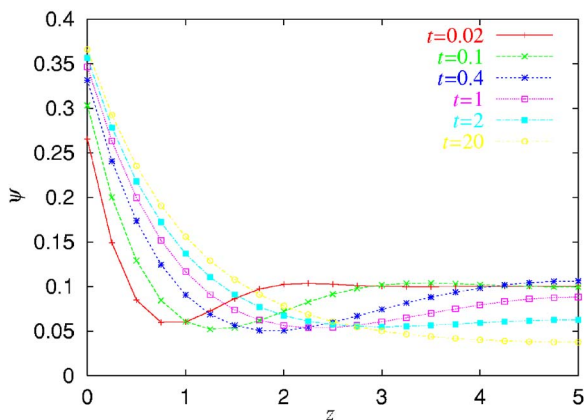

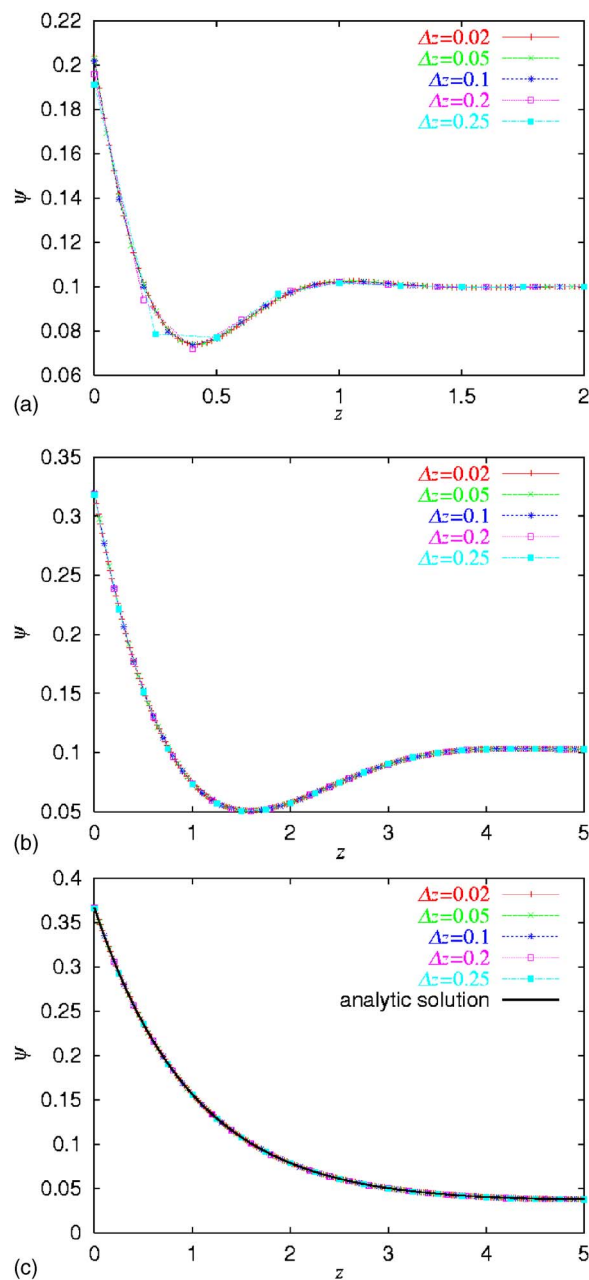FIG. 1. (Color online) Time evolution of the profile of ψ with $\Delta z = 0.25$.

FIG. 2. (Color online) The profiles of ψ for different Δz's at (a) $t = 0.001$, (b) $t = 0.2$, and (c) $t = 20$. In (a), only the region $0 \leq z \leq 2$ is shown, because in $2 \lesssim z \lesssim 8$, $\psi(z)$ stays at its initial value 0.1. In (c), the equilibrium profile calculated analytically in the Appendix is also shown.

very thin surface layer at the initial stage. As time elapses, the profiles for different Δz's become indeed indistinguishable as can be seen in Fig. 2(b), $t = 0.2$, and finally the profiles attain their equilibrium [Fig. 2(c), $t = 20$]. The numerical equilibrium profiles show an excellent agreement with the analytic one obtained in the Appendix, which again supports the validity of our numerical scheme.

To check in a different way how the variation of Δz influences the dynamics of ψ in our numerical scheme, we plot in Fig. 3 the time evolution of the surface order parameter $\psi(0)$ for different Δz's. From Fig. 3(a), we find that at later
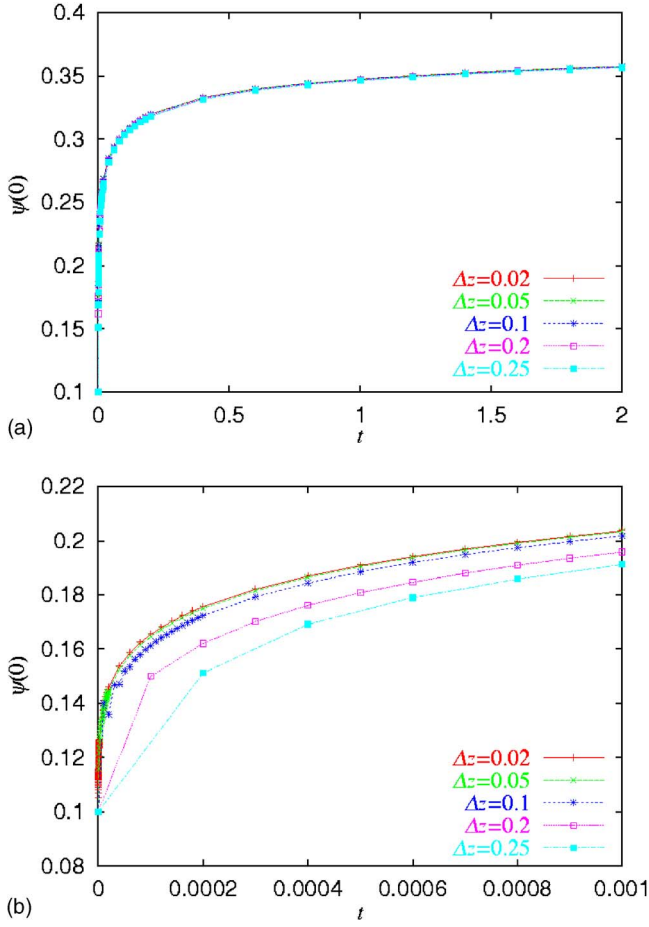
FIG. 3. (Color online) Time evolution of $\psi(0)$ for different Δz's up to (a) $t=2$ and (b) $t=0.001$. In (a), numerical data in $0 < t < 0.0002$ are not shown, which results in an apparent jump of $\psi(0)$ from 0.1 to 0.15. In (b), all the iterations are shown up to $t=0.001$ ($\Delta z=0.25$ and 0.2), $t=0.0002$ ($\Delta z=0.1$), $t=2 \times 10^{-5}$ ($\Delta z=0.05$), and $t=2 \times 10^{-6}$ ($\Delta z=0.02$).

times the numerical data collapse on a single curve, indicating the robustness of our numerical scheme in the late stage, which manifests itself also in Figs. 2(b) and 2(c). A closer inspection of the initial stage in Fig. 3(b) reveals a slight dependence of the evolution of $\psi(0)$ on Δz. However, the data for $\Delta z=0.05$ and 0.02 look like approaching a well-defined asymptotic limit for $\Delta z \to 0$ without suffering from any anomalies. Considering the coarseness of the grids in the cases of $\Delta z=0.25$ and 0.2 for the description of a very thin surface layer, we can still say that the time evolution of $\psi(0)$ is not so far away from the asymptotic limit of $\Delta z \to 0$. It may be worthwhile to point out that in the case of $\Delta z=0.1$ a slight oscillation is observed in the first few iterations, which occurs when the time increment Δt is close to the upper threshold value $(\Delta z)^4/8\kappa$ of the von Neumann criterion (30).

To summarize, we have found from our test calculations that (1) no anomaly is present in our numerical scheme when we decrease the grid spacing Δz, (2) well-defined asymptotic behavior in the limit $\Delta z \to 0$ is observed, and (3) even when Δz is not small, the numerical result is reliable enough as long as the initial stage is not concerned, where very high

numerical resolution is required for the precise description of the spatial variation of ψ.

B. Comparison of our scheme with previous ones

1. The PB model

To discuss the similarities and differences between the PB model and ours, we review the dynamical model of the conserved spin variables originally proposed by Binder and Frisch [19], from which the PB model was derived. When homogeneity in all directions along the wall surface can be assumed so that the system is effectively one dimensional, the kinetic equations for the averaged spin variables $\langle S_n \rangle$ (n being the position index along the surface normal) are written as [19,32]

$$2\tau_s \frac{d}{dt}\langle S_n \rangle = -2\langle S_n \rangle + \langle S_{n+1} \rangle + \langle S_{n-1} \rangle + (1 - \langle S_n \rangle \langle S_{n-1} \rangle)$$

$$\times \tanh\left[\frac{J}{k_B T}(\langle S_{n+1} \rangle - (q-3)\langle S_{n-1} \rangle + (q-3)\langle S_n \rangle\right.$$

$$\left. - \langle S_{n-2} \rangle)\right] + (1 - \langle S_n \rangle \langle S_{n+1} \rangle)$$

$$\times \tanh\left[\frac{J}{k_B T}(\langle S_{n-1} \rangle - (q-3)\langle S_{n+1} \rangle\right.$$

$$\left. + (q-3)\langle S_n \rangle - \langle S_{n+2} \rangle)\right], \tag{31}$$

for $n \geq 2$ in the bulk

$$2\tau_s \frac{d}{dt}\langle S_1 \rangle = -2\langle S_1 \rangle + \langle S_2 \rangle + \langle S_0 \rangle + (1 - \langle S_1 \rangle \langle S_0 \rangle)$$

$$\times \tanh\left\{\frac{J}{k_B T}\left(\langle S_2 \rangle - \left[(q-2)\frac{J_s}{J} - 1\right]\langle S_0 \rangle\right.\right.$$

$$\left.\left. + (q-3)\langle S_1 \rangle - \frac{H_1}{J}\right)\right\} + (1 - \langle S_1 \rangle \langle S_2 \rangle)$$

$$\times \tanh\left[\frac{J}{k_B T}(\langle S_0 \rangle - (q-3)\langle S_2 \rangle + (q-3)\langle S_1 \rangle\right.$$

$$\left. - \langle S_3 \rangle)\right], \tag{32}$$

at the layer adjacent to the surface ($n=1$), and

$$2\tau_s \frac{d}{dt}\langle S_0 \rangle = -\langle S_0 \rangle + \langle S_1 \rangle + (1 - \langle S_1 \rangle \langle S_0 \rangle)\tanh\left\{\frac{J}{k_B T}\left(-\langle S_2 \rangle\right.\right.$$

$$\left.\left. + \left[(q-2)\frac{J_s}{J} - 1\right]\langle S_0 \rangle - (q-3)\langle S_1 \rangle + \frac{H_1}{J}\right)\right\}, \tag{33}$$

at the surface layer ($n=0$). Here τ_s is the characteristic time for the microscopic spin-exchange processes, and q is the coordination number in the bulk. The pair interaction is characterized by J in the bulk, and J_s for a pair of spins involving the surface. The surface field is denoted by H_1.

We define the order parameter at $z=na$ (a is the layer spacing) as $\psi(z,t)=\langle S_n \rangle$. The surface layer is located at $z=0$. Close to the bulk mean-field critical temperature $T_c = qJ/k_B$, the Taylor expansion of Eq. (31) yields

$$2\tau_s \frac{\partial}{\partial t}\psi(z,t) = -a^2 \frac{\partial^2}{\partial z^2}\left[\left(\frac{T_c}{T}-1\right)\psi(z,t) - \frac{1}{3}\frac{T_c}{T}\psi(z,t)^3 \right. $$
$$\left. + \frac{Ja^2}{k_B T}\frac{\partial^2}{\partial z^2}\psi(z,t)\right]. \tag{34}$$

It is important to notice that we have retained explicitly the layer spacing a, while in the usual presentation of the PB model [21], a is assumed to be the unit length. The time evolution of the order parameter at the surface is given, from Eq. (33), by

$$2\tau_s \frac{\partial}{\partial t}\psi(0,t) = \frac{H_1}{k_B T} + \left[(q-2)\frac{J_s}{k_B T}-(q-1)\frac{J}{k_B T}\right]\psi(0,t)$$
$$+ \left.\frac{Ja}{k_B T}\frac{\partial}{\partial z}\psi(z,t)\right|_{z=0}, \tag{35}$$

where terms linear in ψ and up to first order in spatial derivatives have been retained. The Taylor expansion of Eq. (32) for the layer adjacent to the surface ($n=1$) is highly complicated [19]. Therefore, instead, a boundary condition taking care of the conservation of the order parameter at the surface is given in the PB model, which reads

$$\left.\frac{\partial}{\partial z}\left[\left(\frac{T_c}{T}-1\right)\psi(z,t)-\frac{1}{3}\frac{T_c}{T}\psi(z,t)^3+\frac{Ja^2}{k_B T}\frac{\partial^2}{\partial z^2}\psi(z,t)\right]\right|_{z=0} = 0. \tag{36}$$

It should be noticed that the free energy functional in terms of ψ corresponding to the original Hamiltonian for the spin variables can be written as

$$\frac{F[\psi]}{k_B T} = \int_0^\infty \frac{dz}{a}\left[\frac{1}{2}\left(1-\frac{T_c}{T}\right)\psi(z)^2 + \frac{1}{12}\frac{T_c}{T}\psi(z)^4 \right.$$
$$+ \frac{1}{2}\frac{Ja^2}{k_B T}\left(\frac{\partial\psi}{\partial z}\right)^2 \left] + \left(-\frac{H_1}{k_B T}\psi(0) - \frac{1}{2}\left[(q-2)\frac{J_s}{k_B T}\right.\right.$$
$$\left.\left. -(q-1)\frac{J}{k_B T}\right]\psi(0)^2\right). \tag{37}$$

The integrand is the free energy per layer and the integral $\int_0^\infty \frac{dz}{a}$ should be understood as the continuum limit of the summation Σ_n. When we set

$$f_b(\psi(z)) = \frac{1}{a}\left[\frac{1}{2}\left(1-\frac{T_c}{T}\right)\psi(z)^2 + \frac{1}{12}\frac{T_c}{T}\psi(z)^4\right], \tag{38}$$

$$f_s(\psi(0)) = -\frac{H_1}{k_B T}\psi(0) - \frac{1}{2}\left[(q-2)\frac{J_s}{k_B T}-(q-1)\frac{J}{k_B T}\right]\psi(0)^2, \tag{39}$$

together with $\kappa=Ja/k_B T$, $M=a^3/2\tau_s$, and $\Delta z=a$, the PB model (34) and (35) agree with ours [Eqs. (23) and (25)] apart from a numerical factor concerning the surface energy contribution [33] and the contribution from the bulk part in

Eq. (25). We should notice that f_b is, when multiplied by $k_B T$, the bulk free energy "density," which is reflected in the prefactor $1/a$ in Eq. (38). We also emphasize again that in our model the conservation of the order parameter is satisfied in the strict numerical sense, and therefore our model does not include an explicit boundary condition corresponding to Eq. (36), as the original model of Binder and Frisch does not.

From the discussion in this section, we can say that the PB model has a close correspondence to ours when the layer spacing a is identified with the grid spacing Δz in our model. This is a natural consequence of the PB model originating from the lattice model of Binder and Frisch with the lattice spacing a.

We have already seen that the apparent surface mobility [M_s in Eq. (3)] in the discretized system is proportional to $(\Delta z)^{-3}$ from Eq. (25). Therefore a naively-discretized version of the PB model, in particular Eq. (35), does not give a correct result as pointed out by Henderson and Clarke [29], unless the grid spacing Δz is set equal to a. We emphasize again that the PB model implicitly assumes that the lattice spacing (or the distance between adjacent spin layers) is a.

2. The HC model

Henderson and Clarke [29] demonstrated in their simulations that when the grid spacing Δz is varied, consistent results cannot be obtained unless the coefficients in the surface free energy are divided by Δz. Direct comparison between the HC model and ours is unavailable, because they did not present the detailed discretization procedures. But we speculate that the division of the surface free energy by Δz in the HC model corresponds directly to the factor $2/\Delta z$ in our model equations (24) and (25). They arrived at the idea of dividing the surface energy by Δz by comparing the bulk contribution in a numerical lattice cell and the surface contribution at its edge. In the derivation of our model, we argued that the factor $2/\Delta z$ can be regarded as the numerical discretization of the delta function at the surface. Since the HC model can be expressed as the simple model B dynamics, with the driving chemical potential being the functional derivative of the "full" free energy including the surface contribution with a delta function (see eq. (7) of Ref. [29]), our model can be considered quite similar to the HC model. Therefore our argument in Sec. III A can be regarded as a clearer and more rigorous justification of the treatment of the surface energy in the HC model.

IV. CONCLUSION

We have discussed how the so-called model B dynamical equation for a conserved order parameter should be discretized when an impenetrable wall is present. We have presented the appropriate discretization scheme for the dynamics of the order parameter at the surface as well as in the bulk, starting with the form of the free energy with the short-range interaction between the wall surface and the order parameter, and particular attention to the strict conservation of the order parameter in the numerical system. One of the striking features of our model is that the apparent "surface mobility" [M_s in Eq. (3)] depends on the numerical grid

spacing Δz. We have shown analytically and by test calculations that this apparent dependence of the "surface mobility" on Δz does not yield any inconsistency of the numerical results when Δz is varied; the numerical evolution of the order parameter is essentially independent of Δz. Our argument justifies the previous numerical treatment of the model B with a surface by Henderson and Clarke, who divided the coefficients of the surface free energy by Δz in their calculations. The consistency of our model when Δz is varied clearly demonstrates that naive discretization of the surface diffusion equation of the form of (3) is no longer valid. We have also pointed out that our model has a close, although not perfect, correspondence to the familiar model for the same problem proposed by Puri and Binder, when our grid spacing Δz is identified with the lattice spacing of the original Kawasaki-spin system.

In this work we have dealt with the diffusive dynamics of the order parameter and have not included the effect of a hydrodynamic flow. We have also restricted our discussion to the one-dimensional cases. The extension of our model to multidimension is straightforward. The effect of the hydrodynamic flow can be properly included by modifying the flux j, once the profile of the flow velocity for a given order parameter profile is appropriately calculated. Therefore we believe that our model for the dynamics of a conserved order parameter in the presence of walls provides a firm basis for the numerical treatment of the dynamics of a fluid in the vicinity of a wall surface when the surface free energy is explicitly given.

ACKNOWLEDGMENTS

APPENDIX: EQUILIBRIUM PROFILE FOR THE TEST PROBLEM IN SECTION III A 2

The free energy for the present problem is

$$F[\psi(z)] = \int_0^L dz \left[f_b(\psi(z)) + \frac{1}{2}\kappa\left(\frac{\partial}{\partial z}\psi(z)\right)^2 \right] + f_s(\psi(0))$$
$$+ f_s(\psi(L)). \quad (A1)$$

Minimization of Eq. (A1), i.e., $\delta F / \delta\psi = \mu$, yields

$$f_b'(\psi(z)) - \kappa\frac{\partial^2\psi(z)}{\partial z^2} = \mu \quad (0 < z < L), \quad (A2)$$

$$-\kappa\frac{\partial\psi}{\partial z}(0) + f_s'(\psi(0)) = 0 \quad (z = 0), \quad (A3)$$

$$\kappa\frac{\partial\psi}{\partial z}(L) + f_s'(\psi(L)) = 0 \quad (z = L). \quad (A4)$$

Since we have chosen $f_b'(\psi) = a\psi$, Eq. (A2) is readily integrated to give

$$\psi(z) = \frac{\mu}{a} + A_1 e^{-z/\xi} + A_2 e^{z/\xi}, \quad (A5)$$

where $\xi \equiv \sqrt{\kappa/a}$. Now we have three unknown parameters: A_1, A_2, and μ. Equations (A3) and (A4) serve as the two of the three conditions that determine the unknowns. The last condition comes from the conservation of ψ, Eq. (4). In the present problem, it reads

$$\psi_{\text{init}} L = \int_0^L dz\,\psi(z) = \frac{\mu L}{a} - A_1\xi(e^{-L/\xi} - 1) + A_2\xi(e^{L/\xi} - 1).$$
$$(A6)$$

Since from our choice $f_s'(\psi) = b(\psi - \psi_{s0})$, Eqs. (A3), (A4), and (A6) constitute a set of linear equations for our three unknowns. Although it can be readily solved, the explicit expression for the solution is rather lengthy and not essential to our discussion. Therefore we merely mention here that for the present choice of the parameters, i.e., $a = 1$, $b = 2.5$, $\kappa = 1$, $L = 10$, $\psi_{s0} = 0.5$, and $\psi_{\text{init}} = 0.1$, A_1, A_2, and μ are given by

$$A_1 = \frac{1}{3 + 2e^{-10}}, \quad (A7)$$

$$A_2 = \frac{e^{-10}}{3 + 2e^{-10}}, \quad (A8)$$

$$\mu = \frac{1 + 4e^{-10}}{10(3 + 2e^{-10})}, \quad (A9)$$

which yield the equilibrium profile

$$\psi(z) = \frac{1 + 4e^{-10}}{10(3 + 2e^{-10})} + \frac{2}{3e^5 + 2e^{-5}}\cosh(z - 5). \quad (A10)$$

It is clear that the profile of Eq. (A10) is symmetric about the center $z = 5$.

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

[2] *Fluid Interfacial Phenomena*, edited by C. A. Croxton (Wiley, New York, 1986).

[3] S. Dietrich, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and J. Lebowitz, Vol. 12 (Academic Press, London, 1988).

[4] M. Schick, in *Liquids at Interfaces, Les Houches, Session XLVIII, 1988*, edited by J. Charvolin, J. F. Joanny, and J. Zinn-Justin (Elsevier Science Publishers, New York, 1990).

[5] P. G. de Gennes, F. Brochard-Wyart, and D. Quere, *Capillarity and Wetting Phenomena: Drops, Bubbles, Pearls, Waves* (Springer Verlag, New York, 2004).

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

[7] H. Nakanishi and M. E. Fisher, Phys. Rev. Lett. **49**, 1565 (1982); R. Lipowsky, *ibid.* **49**, 1575 (1982); R. Lipowsky and W. Speth, Phys. Rev. B **28**, 3983 (1983).

[8] For reviews, see, e.g., S. Puri and H. L. Frisch, J. Phys.: Condens. Matter **9**, 2109 (1997); K. Binder, J. Non-Equilib. Thermodyn. **23**, 1 (1998); H. Tanaka, J. Phys.: Condens. Matter **13**, 4637 (2002); S. Puri, *ibid.* **17**, R101 (2005).

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

[10] P. Wiltzius and A. Cumming, Phys. Rev. Lett. **66**, 3000 (1991).

[11] H. Tanaka, Phys. Rev. Lett. **70**, 53 (1993); H. Tanaka, *ibid.* **70**, 2770 (1993); Europhys. Lett. **24**, 665 (1993).

[12] G. Krausch, C. A. Dai, E. J. Kramer, and F. S. Bates, Phys. Rev. Lett. **71**, 3669 (1993); Macromolecules **27**, 6768 (1994).

[13] B. Q. Shi, C. Harrison, and A. Cumming, Phys. Rev. Lett. **70**, 206 (1993).

[14] M. Geoghegan, H. Ermer, G. Jungst, G. Krausch, and R. Breen, Phys. Rev. E **62**, 940 (2000); M. Geoghegan and G. Krausch, Prog. Polym. Sci. **28**, 261 (2003).

[15] H. Wang and R. J. Composto, J. Chem. Phys. **113**, 10386 (2000); Phys. Rev. E **61**, 1659 (2000).

[16] H. Jinnai, H. Kitagishi, K. Hamano, Y. Nishikawa, and M. Takahashi, Phys. Rev. E **67**, 021801 (2003).

[17] P. C. Hohenberg and B. I. Halperin, Rev. Mod. Phys. **49**, 435 (1977).

[18] D. Jacqmin, J. Comput. Phys. **155**, 96 (1999); J. Fluid Mech. **402**, 57 (2000).

[19] K. Binder and H. L. Frisch, Z. Phys. B: Condens. Matter **84**, 403 (1991).

[20] K. Kawasaki, Phys. Rev. **145**, 224 (1966); **148**, 375 (1966); **150**, 285 (1966).

[21] S. Puri and K. Binder, Phys. Rev. A **46**, R4487 (1992); Phys. Rev. E **49**, 5359 (1994).

[22] J. F. Marko, Phys. Rev. E **48**, 2861 (1993).

[23] S. Puri and K. Binder, J. Stat. Phys. **77**, 145 (1994).

[24] M. A. Vaksman and W. E. McMullen, Phys. Rev. E **49**, 4724 (1994).

[25] B. P. Lee, J. F. Douglas, and S. C. Glotzer, Phys. Rev. E **60**, 5812 (1999).

[26] H. Tanaka and T. Araki, Europhys. Lett. **51**, 154 (2000), where the PB model was extended to take into account the hydrodynamic effect.

[27] S. Puri and K. Binder, Phys. Rev. Lett. **86**, 1797 (2001).

[28] S. K. Das, S. Puri, J. Horbach, and K. Binder, Phys. Rev. E **72**, 061603 (2005).

[29] I. C. Henderson and N. Clarke, Macromol. Theory Simul. **14**, 435 (2005).

[30] W. H. Press, S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery, *Numerical Recipes in C*, 2nd ed. (Cambridge University Press, Cambridge, 1992).

[31] The factor 2 in Eq. (16) and our discretized δ function is attributed to the fact that ψ_0 describes the state of the region with the width $\Delta z/2$, i.e., $0 \leq z < \Delta z/2$, while all the other ψ_i's govern a region with double the width, i.e., $(i-1/2)\Delta z \leq z < (i+1/2)\Delta z$.

[32] S. Puri and H. L. Frisch, J. Chem. Phys. **99**, 5560 (1993).

[33] The difference in the numerical factor between the PB model and ours arises from the implication of the conservation in each model: in our model we consider that $(1/2)\psi_0 + \Sigma_{i=1}^{\infty}\psi_i$ is constant with time [Eq. (19)], while in the model of Binder and Frisch $\Sigma_{n=0}^{\infty}\langle S_n \rangle$ is conserved.