On the numerical treatment of the dynamics of a conserved order parameter in the presence of impenetrable walls

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保存する秩序変数の時間発展を記述する方程式を連続体シミュレーションとして数値実装する際，秩序変数と局所的に相互作用し，秩序変数の法線方向の流れを許さない壁をどのように扱うべきかを考察する．壁と秩序変数との相互作用の結果，数値モデルには自明でない形で格子間隔Δが陽に現れることを示す．解析的議論と簡単な数値計算により，Δが漸近的にゼロに近づく極限においても，このモデルに特異性は現れず矛盾がないことを示すことができる．

How a liquid in a vapor, or a mixture of liquids, behaves in the vicinity of solid surfaces or walls has long been an important problem in fundamental science as well as in applications. Typical examples include wetting phenomena and surface-directed phase separation. In many cases such phenomena can be described theoretically in terms of a conserved order parameter $\psi(\boldsymbol{r})$. In a semi-infinite one-dimensional system where a wall is located at $z = 0$, the free energy of the total system can be formally written in terms of ψ as

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

where $f_{\rm b}$ is the local free energy density in the bulk and f_s represents the localized interaction between ψ and the wall. When the effect of hydrodynamic flow is neglected and only a diffusion process for the relaxation of ψ is considered, the equation of motion for ψ in the bulk reads

$$\frac{\partial}{\partial t}\psi(z,t) = \frac{\partial}{\partial z}\left(M \frac{\partial}{\partial z} \frac{\delta F}{\delta \psi(z)} \right), \tag{2}$$

where M is the mobility that can be dependent on ψ and z. Although eq. (2) is well-defined and readily discretized in the bulk, the time evolution of the order parameter at the wall, $\psi(0)$, is not trivial and cannot be described straightforwardly by eq. (2). The aim of the present study is to discuss how the dynamics of $\psi(0)$ should be numerically treated and to compare our treatment with the previous ones for the same problem.

We discretize the system with the spacing Δ and define $\psi_i = \psi(i\Delta)$ for $i \geq 0$. The free energy (1) is discretized accordingly using a trapezoidal rule and the discretized version of the

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conservation of ψ reads $(d/dt)\sum_{i=0}^{\infty}(\psi_i+\psi_{i+1})/2=0$. When we define the discretized functional derivative of F from the bulk contribution as $\delta F_{\rm b}/\delta\psi_i = f_{\rm b}'(\psi_i)-\kappa(\psi_{i-1}-2\psi_i+\psi_{i+1})/\Delta^2$ for $i\geq 1$ and $f_{\rm b}'(\psi_0)-\kappa(\psi_0-2\psi_1+\psi_2)/\Delta^2$ for $i=0$, we can show that the equations for the time evolution of ψ_i's in the case of $M=1$ can be written as[1]

$$\frac{\partial}{\partial t}\psi_i = \frac{1}{\Delta^2}\left(\frac{\delta F_{\rm b}}{\delta\psi_{i-1}}-2\frac{\delta F_{\rm b}}{\delta\psi_i}+\frac{\delta F_{\rm b}}{\delta\psi_{i+1}}\right)\ (i\geq 2), \tag{3}$$

$$\frac{\partial}{\partial t}\psi_1 = \frac{1}{\Delta^2}\left(\frac{\delta F_{\rm b}}{\delta\psi_0}-2\frac{\delta F_{\rm b}}{\delta\psi_1}+\frac{\delta F_{\rm b}}{\delta\psi_2}+\frac{2}{\Delta}\left\{-\kappa\frac{-3\psi_0+4\psi_1-\psi_2}{2\Delta}+f_{\rm s}'(\psi_0)\right\}\right), \tag{4}$$

$$\frac{\partial}{\partial t}\psi_0 = \frac{2}{\Delta^2}\left(-\frac{\delta F_{\rm b}}{\delta\psi_0}+\frac{\delta F_{\rm b}}{\delta\psi_1}-\frac{2}{\Delta}\left\{-\kappa\frac{-3\psi_0+4\psi_1-\psi_2}{2\Delta}+f_{\rm s}'(\psi_0)\right\}\right). \tag{5}$$

We can easily find that eq. (3) is the discretized version of eq. (2) and that the factor $1/\Delta^2$ arises from the discretization of the Laplacian. The factor $2/\Delta$ associated with the surface contribution in eqs. (4) and (5) is not trivial, but it can be considered as originated from the δ function implicit in $f_{\rm s}$. The necessity of including a factor Δ^{-1} in the surface contribution has already been argued heuristically by Henderson and Clarke[2]. One might suspect that this factor could yield some anomaly in the limit $\Delta\to 0$. We can show analytically using a discrete Fourier transform that such anomaly does not occur and simple test calculations also confirm this[1].

Finally we comment on the correspondence of our model to the widely-used continuum model by Puri and Binder (PB)[3] for the same problem. The PB model originates from the Kawasaki spin-exchange lattice model in the presence of walls[4]. Our model has direct correspondence to the PB model if Δ is identified with the spacing of the original lattice model, and the same grid spacing is used for the discretization of the PB model. On the contrary, a naively-discretized version of the PB model without taking care of the choice of the grid spacing cannot give a correct result. We also notice that in our model, the explicit no-flux boundary condition at the wall is not necessary, because we deal with the conservation of ψ in the rigorous manner.

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