Preservation of Isotropy at the Mesoscopic Stage of Phase Separation Processes

Hiroyuki TOMITA

Department of Physics, College of General Education, Kyoto University, Kyoto 606

(Received August 6, 1990)

A practical conservation law related to isotropy is proposed for the deterministic Cahn-Hilliard equation, i.e., the order parameter conserving TDGL model. In order to examine it a dipole moment of the order parameter distribution in a two dimensional system is numerically calculated by using the cell-dynamics method and is shown to remain microscopic even at the mesoscopic, scaling stage of the phase separation process. This fact is related to the $k^4$ law in small wavenumber region of the scaling form of the structure function. The characteristic length scale is also calculated directly in two ways, and the $t^{1/3}$ law for its growth at the mesoscopic stage is confirmed with good accuracy.

§ 1. Introduction

Since the scaling law in the phase separation process is proposed, many works are devoted to confirming it experimentally and to revealing its origin theoretically. However, the overall scaling form of the correlation function or the structure function has not been determined analytically, except for the so-called Porod tail in the large wavenumber region due to development of sharp interfaces separating two phases in the late stage of the process. Recently the small wavenumber region, where we have naively believed the $k^2$ dependence because of the order parameter conservation, is re-examined, and a new, $k^4$ law is claimed in some cases. The purpose of the present paper is to discuss it in connection with some conservation law with respect to the isotropy of the system subjected to the simple Cahn-Hilliard equation, i.e., the isotropic, order parameter conserving TDGL equation. We assume that the concerned mesoscopic stage, where the scaling law of the spatial pattern is realized, should have the following properties:

1) No longer microscopic. We have well-developed interfaces which separate two phases sharply and have smooth curvatures everywhere.

2) Not macroscopic yet. Though the local heterogeneity has been developed, the initial homogeneity and isotropy are preserved globally. That is, the spatial pattern is random and still has rotational symmetry as well as translational one.

It is shown in § 2 that the $k^2$ term in the structure function should disappear when this isotropy condition is completely satisfied. These are examined numerically in § 3 using a two dimensional cell dynamics model which has been introduced by Oono et al. into the present problem.

§ 2. Phenomenological considerations

Let $\{u(r)\}$ be a dimensionless order parameter which corresponds to the local concentration of binary system with a spatial average

Progress of Theoretical Physics, Vol. 85, No. 1, January 1991
\[ \bar{u} = \frac{1}{V} \int u(r) \, dV, \] (1)

where \( V \) is the volume of the system. Then the correlation function and the structure function are defined by

\[ g(r) = \frac{1}{V} \int \rho(r_1) \rho(r_1 + r) \, dV, \] (2)

and

\[ S(k) = \int \exp(ik \cdot r) g(r) \, dV, \] (3)

where a new order parameter variable

\[ \rho(r) = u(r) - \bar{u} \] (4)

is used. In the present case of a conserved order parameter the spatial average \( \bar{u} \) defined by Eq. (1) is a dynamical constant and we have

\[ \int \rho(r) \, dV = 0 \] (5)

by definition. As usual it can be expected that the correlation length is finite except for the critical case, that is

\[ \int r^n g(r) \, dV = \text{finite} \]

for any non-negative integer \( n \), and if the system size tends to infinite \( (V \to \infty) \), the structure function defined by Eq. (3) can be written in the following power expansion form:

\[ S(k) = -\frac{k^2}{2!d} \int r^2 g(r) \, dV + \frac{3k^4}{4!d(d+2)} \int r^4 g(r) \, dV + \cdots, \] (6)

where \( S(k) \) is spherically averaged over the direction of \( k \) and denoted simply by \( S(k) \) and \( d \) is the dimensionality of the system. The constant term does not appear in the expansion because

\[ \int g(r) \, dV = \frac{1}{V} \int \rho(r) \rho(r_1 + r) \, dV \, dV = 0 \] (7)

by Eq. (5). Similarly the integral of the \( k^2 \) term in Eq. (6) is rewritten as

\[ \int r^2 g(r) \, dV = \frac{1}{V} \int (r_1 - r_2)^2 \rho(r_1) \rho(r_2) \, dV \, dV = -\frac{2}{V} \left( \int r \rho(r) \, dV \right)^2, \] (8)

where Eq. (5) is used again. Then this term should disappear too, if the system
Preservation of Isotropy at the Mesoscopic Stage

preserves complete rotational symmetry. Note that the vector quantity defined by the integral in the last expression in Eq. (8)

\[ \mathbf{p} = \int \rho(r) dV, \]  

is a ‘dipole moment’ of the ‘neutral charge’ system \( \{ \rho(r) \} \). In other words, \( \mathbf{p}/V \) is proportional to the displacement vector \( \mathbf{R}_+ - \mathbf{R}_- \), where \( \mathbf{R}_+ \) (\( \mathbf{R}_- \)) is the center of positive (negative) charge region: Suppose that the order parameter is saturated almost everywhere, i.e., \( \rho(r) = \rho_+ \) or \( \rho(r) = \rho_- \). Then it is easily shown that

\[ \mathbf{p}/V = \phi(1-\phi)\Delta \mu(\mathbf{R}_+ - \mathbf{R}_-), \]

where \( \phi \) is the volume fraction of positive charge region and \( \Delta \mu \) the so-called order parameter gap defined by \( \Delta \mu = \rho_+ - \rho_- \). \( \mathbf{R}_+ \) and \( \mathbf{R}_- \) are defined by

\[ \mathbf{R}_+ = (1/\phi V) \int_r dV \quad \text{and} \quad \mathbf{R}_- = (1/(1-\phi)V) \int_r dV, \]

where each integral is restricted in the respective charge region.

Of course this dipole moment is not a dynamical conservative like the total charge, since in the final, true equilibrium state the two phases would be macroscopically separated, i.e., \( \mathbf{p}/V \) would be of the order of the linear dimension of the system. It is shown, however, that this is a slowly varying quantity which obeys a continuity equation as follows: Let us start with the well-known phenomenological equations,

\[ \frac{\partial \mu}{\partial t} = \frac{\partial \rho}{\partial t} = -\text{div} \mathbf{j} \quad \text{and} \quad \mathbf{j} = -L \text{grad} \mu, \]

where \( L \) is the transport coefficient and \( \mu \) the local chemical potential, whose explicit expression is unnecessary here and to be introduced in the next section. Define the dipole moment density by

\[ \mathbf{P}(r) = r \rho(r). \]

Then combining Eqs. (11) and (12) a continuity equation for the vector quantity \( \mathbf{P} \)

\[ \frac{\partial}{\partial t} P_a = -\sum_b \frac{\partial}{\partial x_b} (x_a j_b + L \mu \delta_{ab}), \quad (a, b = x, y, z) \]

is obtained. Integrating Eq. (13) with use of the natural boundary condition (NBC)

\[ \mathbf{j} \cdot \mathbf{n} = 0, \]

which assures the conservation of neutrality

\[ \frac{d}{dt} \int \rho(r) dV = -\int_S \mathbf{j} \cdot \mathbf{n} dS = 0, \]

one finds

\[ \frac{d\mathbf{P}}{dt} = -(1/V) \int_S L \mu \mathbf{n} dS, \]
where
\[ \bar{P} = \frac{1}{V} \int \rho(r) dV = \frac{p}{V}, \] (16)

and S is the boundary surface and S its area. Compared to the charge conservation Eq. (14), the right-hand side of Eq. (15) cannot be eliminated. It depends on the system size as a surface effect. However this surface contribution is formally of the order of \( S/V \) and in addition its integrand \( \mu n \) is a random vector. Then \( \bar{P} \) could be a slowly varying variable for sufficiently large random pattern systems and we could expect the isotropic mesoscopic state as is mentioned in § 2. Roughly speaking, at least if \( \bar{P}^2 \) remains of the order of \( 1/V \), the coefficient of the \( k^2 \) term in the expansion Eq. (6), which is rewritten as \( VP^2/d \), can be neglected at the mesoscopic stage where the characteristic length scale becomes semimacroscopic. This condition is examined in more detail in the next section using numerical results.

It should be noted that we cannot get any similar conclusion on the coefficient of the \( k^4 \) term. The non-zero value of the elements of the second moment tensor which appear in the \( k^4 \) coefficient, e.g.,
\[ \int (x^2 + y^2) \rho(r) dV \] (17)
for \( d = 2 \) is compatible with isotropy. As is clearly demonstrated in the cell dynamics version, the elementary processes of the Cahn-Hilliard equation are isotropic. Apparently the dipole moment is conserved by the single elementary process shown in Fig. 1 except at the boundary cell, but the second moment such as Eq. (17) is not conserved.

\[ \begin{array}{c}
| & | & | \\
| i \rightarrow j & = & j \rightarrow i \\
| & | & |
\end{array} \]

Fig. 1. The order parameter conserving net current between neighboring cells is composed of a couple of isotropic elementary processes. Original illustration is found in Ref. 7).

§ 3. The cell dynamics model and numerical results

The cell dynamics (CD) model is essentially an efficient discretization of the deterministic hydrodynamic equation like Eq. (11). Let us consider the simplest case of the critical quench \( \bar{u} = 0 \) of the symmetric system, where the chemical potential \( \mu \) in Eq. (11) is given by
\[ \mu = df/du - DP^2u \]
and \[ f(u) = -au^2/2 + gu^4/4. \]

Here \( f(u) \) is the local free energy density for the single phase state and \( D \) the coefficient of surface energy. Then the discretized version of Eq. (11) with respect to time \( t \) is written as

\[ u(r, T+1) - u(r, T) = \frac{1}{2} \left( df/du - D \right) \nabla^2 u, \]

where the potential term \( df/du \) is to be replaced by an efficient map function with attractors at \( \pm u_0 \) (where \( df/du = 0 \)) corresponding to the first order phase transition. Here we employed the hyperbolic tangent map, \( \frac{df}{du} = u - \tanh u \) \( (a > 1) \)

(19)

The second point of the CD method is to discretize the space into cells and to represent the Laplacian in Eq. (18) by interactions between the near-neighboring cells. For example, in the case of the two dimensional square cell system, one may write it as

\[ \nabla^2 u(r) = \frac{1}{1 + \varepsilon^2} \left\{ \sum_{nn} u(r + a) + \varepsilon \sum_{nn} u(r + a') - 4(1 + \varepsilon) u(r) \right\}, \]

(20)

where \( \varepsilon \) is an arbitrary weight parameter and \( nn \) and \( nnn \) denote the nearest and the next-nearest neighbors, respectively. The value \( \varepsilon = 0.5 \) is chosen by the original authors. They say this choice gives the best isotropy of the patterns empirically. The Fourier representation of the Laplacian is suggestive for this fact. One may find approximately the best overall isotropy for \( \varepsilon = 0.5 \) in Fig. 2.

Fig. 2. Contours of the Fourier representation of the discretized version of the Laplacian defined by Eq. (20).

We simulated a 256 X 256 cell system of the square lattice using the parameters \( L = 0.25, D = 0.125, a = 1.3 \) and \( \varepsilon = 0.5 \). The value \( a = 1.3 \) gives stable attractors \( df/du = 0 \) at \( \pm u_0 = \pm 0.9776\ldots \). Note that the definitions of the parameters \( L \) and \( D \) differ from those of Ref. 7) because of the difference in the coefficient in Eq. (20). Here the coefficient is introduced so that the Fourier representation of the Laplacian for small wavenumber \( k \) coincides with \( -k^2 \) for any \( \varepsilon \).

A typical pattern development in an isotropic system is shown in Fig. 3(a), where the initial state \( (T = 0) \) is given by a uniform, random distribution of equally weighted \( \pm 0.001 \) values of \( u \). The boundary condition is NBC. Five runs are performed with the same conditions. The dipole moment vector \( \vec{P} \) is found to fluctuate as a Brownian motion, but the magnitude \( |\vec{P}| \) remains of the order less than \( 10^{-2} \) at all times \( T \leq 20000 \) and in all five runs. Here the unit of length is the cell dimension. The value
Fig. 3. Pattern development (a) in an isotropic system and (b) in an anisotropic system starting from an initial state with uniform concentration gradient. The region \( u < 0 \) is painted black.
|P|<10^{-2} in this unit with the definition Eq. (16) or more explicitly Eq. (10) is very astonishing compared to the spatial scale of the patterns (~10 as is shown below) of the last state in Fig. 3(a). In order to emphasize this fact of isotropy preservation, a system with a contrasting initial state, i.e., a state with uniform gradient of the concentration from \( \phi=0 \) to \( \phi=1 \) in the \( x \) direction is simulated, and the pattern development is shown in Fig. 3(b). Even in this case the variation of \( P_x \) is found to be merely 1% (from \( P_x=42.0 \) at \( T=0 \) to \( P_x=42.5 \) at \( T=20000 \)).

The characteristic length in the mesoscopic stage is defined by inverse of the interface density^9

\[ A=(1/V)\int da . \tag{21} \]

This quantity is directly calculated in two ways: (1) The perimeter length, i.e., the number of the cell sides where the sign of the order parameter \( \alpha \) changes. (2) The degree of the order parameter sub-saturation defined by

\[ A=(1/V)\int(1-\alpha(r)^2/\alpha_0^2)dV'. \tag{22} \]

Both are shown in Fig. 4 for one run of the isotropic case. The results of all five runs are found exactly equivalent to this figure. In addition the late behaviors at \( T \approx 500 \) do not depend on the initial amplitude \( \alpha_i \) (=0.001 for the case shown in Fig. 3) at least within the extension of examined values \( \alpha_i=0.1 \) and \( \alpha_i=0.000001 \). Thus the behavior of \( A \) is fairly systematic. As is seen in Fig. 4 the \( t^{-1/3} \) law is well established in the range from \( T \approx 500 \) to \( T=20000 \). This range of time itself is the mesoscopic or the scaling stage. Note that the difference in dimension between both definitions of \( A \) corresponds to the interface thickness and the ratio between them reads about 1.5 cell size in the present calculation.

Now let us discuss the scaling form of the structure function. The Porod tail in the large \( k \) region for \( d=2 \) is given by^10

\[ S(k) \sim 2(\Delta \alpha)^2 A/k^3 , \tag{23} \]

where the order parameter gap \( \Delta \alpha \) is to be replaced by \( 2\alpha_0 \) in the present case. The interface density \( A \) defined by Eq. (22) has a dimension of inverse of length and used as the characteristic wavenumber. Define the scaling function by

\[ F(Q) = \frac{A^2}{2(\Delta \alpha)^2} S(AQ) , \tag{24} \]
so that the large $Q$ part is normalized as

$$F(Q) \approx 1/Q^3 \quad \text{for} \quad Q \gg 1,$$

and write the small $Q$ part corresponding to Eq. (6) as

$$F(Q) = C_2 Q^2 + C_4 Q^4 + \cdots ,$$

where the dimensionless coefficients for $d=2$ are defined by

$$C_2 = V P^2 A^4 / 16 u_0^2 ,$$

and so on. Note that the formal expansion Eq. (6) (or Eq. (26)) is possible only at $V \to \infty$ limit as is mentioned in § 2. In order to obtain some information for an infinite system from the present calculations for a finite system, one has to perform averaging over infinite number of runs. In fact the coefficients of the power expansion for an infinite system are shown to be given by simple arithmetic means of those over infinite set of equal finite systems, whenever each of the latter is sufficiently large and can be regarded as a mutually independent partial system of the former.

The dimensionless coefficients $C_2$ and $C_4$ are directly obtained by calculating the corresponding multipole moments of the spatial distribution of the order parameter instead of calculating the structure function itself. The numerical results given by five runs for a $256 \times 256$ isotropic system show that the coefficient $C_2$ in Eq. (26) is negligibly small, i.e.,

$$C_2 < 0.001 ,$$

in the whole range of simulations $T \leq 20000$, and $C_4$ is rather fluctuating but remains of the order of unity, i.e.,

$$C_4 = 0.2 \sim 0.4 ,$$

in the scaling region $T = 500 \sim 20000$ as is shown in Fig. 5. Then $Q^4$ term becomes

![Fig 5. The dimensionless coefficient $C_4$ for five runs. The broken curve is the arithmetic mean of them.](https://academic.oup.com/ptp/article-abstract/85/1/47/1856694)
dominant at $Q > 0.05$. From the present data, however, we cannot bring a definite conclusion whether the coefficient $C_4$ is constant or not, that is, whether the small wavenumber region of the structure function obeys the same scaling law as that in the large wavenumber region or not.

§ 4. Concluding remarks

Using a CD model for the deterministic Cahn-Hilliard equation, or the order parameter conserving TDGL model, it is numerically shown that the initial isotropy of the system is practically conserved. Then for sufficiently large system we have well-defined mesoscopic stage where the characteristic length of patterns is no longer microscopic but the global spatial asymmetry remains within microscopic scale yet.

The thermal noise is neglected except for randomness of the initial configuration in the present work. A preliminary result of the present work is reported in Ref. 11, where a kinetic Ising model is used, that is, the thermal noise is included in principle. Though the dipole moment is not conserved in each elementary process of spin exchange, it is also shown there that its magnitude remains of the order of unity (=lattice spacing) up to the stage where the characteristic length $A^{-1}$ of patterns becomes of the order of 10 lattice spacings. Thus the initial isotropy is well preserved in spite of the thermal noise. A weak point is that the $t^{1/3}$ scaling law has not been found yet at that stage. The CD model may be interpreted as a coarse grained or smoothed version of the kinetic Ising model and is an efficient method to attain the scaling stage. A significant effect of the thermal noise is the persistent local roughness of the interface. Disregard of it does not seem fatal to the present arguments based on the global statistical quantities.

The reasoning of the $k^4$ dependence of the scaled structure function in the small wavenumber range is simple. The argument is based on the preservation of the initial isotropy described by a continuity equation for the dipole moment, which is derived by using the Cahn-Hilliard equation. In fact, large spontaneous fluctuations of the dipole moment are found in another model of a non-conserved order parameter. Thus the argument itself cannot be applied to other cases such as fluid systems which include the hydrodynamical motions. An interesting fractional exponent $k^{2\nu}$ ($0<\nu<2$) is reported in the case of long range interactions. This is also beyond the present simple argument.

Concerning the overall scaling from the small wavenumber region to the large wavenumber region, five runs are not enough to bring a definite conclusion. The dimensionless scaled coefficient $C_t$ shown in Fig. 5 seems weakly increasing with time in one view. We need to simulate larger system and more runs to confirm it.

References

Note added in proof: Let us discuss the effect of thermal noise on the scaling property of the $k^2$ term explicitly. If the thermal noise is included in Eq. (11), the evolution equation for the second moment of the correlation function $g(r, t)$ is shown to be written as

$$\frac{\partial}{\partial t} \int r^2 g(r, t) dV = -4dLk_B T,$$

where an infinite system is assumed, i.e., the boundary effect is neglected. Then the small wavenumber part of the structure function is approximated by

$$S(k, t) \approx (2Lk_B T)tk^2,$$

with use of Eq. (6). Finally the dimensionless coefficient $C_2$ of the scaling function $F(Q)$ is estimated as follows:

$$C_2(t) = (2Lk_B T)t^{d+2} - t^{-(d-1)/3}.$$

That is, the $Q^2$ term should be negligible at the scaling stage.