Effect of nonlinearity of the evolution equation on the spinodal decomposition process in alloys

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The spinodal decomposition process is usually described by nonlinear evolution equations. One of them is the Langer–Bar-on–Miller (LBM) theory that describes the time evolution of a double-Gaussian probability distribution function of composition. In the present study, LBM theory was modified in terms of composition dependence of mobility. The reformulated analytical expression was quantitatively applied to the realistic structure change. In fact we investigated the nonlinear effect on phase decomposition using computer simulations based on the present modified LBM theory and compared the result with the original LBM theory. It was made clear that the additional nonlinear terms played a dominant role in the phase decomposition process. Especially, when the probability distribution function becomes broader in the early stage, the new nonlinear terms contribute to the rapid phase decomposition. [S0163-1829(98)09041-9]

I. INTRODUCTION

In general, the phase decomposition phenomena in metallic alloy systems can be expressed as a change of space distribution of solute composition, which is represented by the evolution equation based on the diffusion equation.[1,2] In the equation, the state of a system needs to be described by the free energy relating to the space distribution of composition. In 1960s, Cahn analyzed theoretically the time evolution of composition fluctuation during the spinodal decomposition using the diffusion equation with Ginzburg-Landau-type free energy,[3] and obtained its analytical solution by making a linear approximation. However, the solution known as Cahn's linear spinodal theory does not hold at the late stage of phase decomposition because the nonlinear effects become more important there. After this, many researchers proposed various theories considering some nonlinear effects.[4–6] For example, Langer *et al.* derived the motion equation of the structure factor from the master equation using the spatial correlation and the probability distribution of the configuration of composition.[7–10]

Recently, the computer simulation on a time-dependent Ginzburg-Landau–type evolution equation and the other modified forms[11–16] are applied quite extensively in order to study the time evolution of phase decomposition. In this type of method, the change of space distribution of composition in real space is given by the straightforward repeatable numerical calculation. The result is directly compared with the TEM images of the microstructure and gives effective insight on the anisotropy of structure that generates in the system with anisotropic elastic energy or directional external-field effects.[13–16] But, it is difficult to evaluate visibly the positive nonlinear effect on the phase decomposition using this type of equation because the effect in the whole system was expressed as only a result of transmission of local effects.

One of nonlinear effects in a realistic metallic system is caused by the composition dependence of mobility[10,17,18] owing to local thermal stability defined by local atomic configu-

ration. Some researchers carried out the computer simulations based on the Cahn-Hilliard equation with a variable mobility so as to investigate the time evolution of fluctuation structure in real space.[5,19] Moreover, the analytical static solution of the equation with mobility, which was derived from the Ising model, was also formulated.[20] However, the direct effect of the nonlinear terms due to a variable mobility on phase decomposition has been little focused on. In order to study the nonlinearity of spinodal decomposition, we have adopted Langer–Bar-on–Miller theory[10] (LBM theory) as a starting reference that has some advantages. First, the theory treats the probability distribution function of composition, which is important in the phase decomposition with regard to statistical handling. Second, in a series of the equations of LBM theory, there are the nonlinear terms expressing the average effects of the whole system, by which it is possible to estimate quantitatively the effect of the nonlinearity. However, the theory needs to be modified, especially in conjunction with the composition dependence of mobility.[13] In this paper, we treated the expansion of LBM theory by considering a variable mobility and carried out the numerical calculation of structure change, and then finally made clear the role of newly introduced nonlinear terms.

II. THEORETICAL CONSIDERATION

The phenomenological composition dependence of mobility on the real binary alloys is known as Darken's equation on mutual diffusion constant as follows:[17]

$$M(c) = [M_A c + (1-c)M_B]c(1-c), \quad (2.1a)$$

where c is composition of solute atom, M_X is the mobility of X atom. Equation (2.1a) is rewritten in polynomial equation form about a difference between local composition within a coarse-graining volume and average composition of whole system $u(\mathbf{r}) = c(\mathbf{r}) - c_0$ as follows:

$$\bar{M}(u) = \bar{M}_0 + \bar{M}_1 u + \bar{M}_2 u^2 + \bar{M}_3 u^3, \quad (2.1b)$$

where $\bar{M}_n$'s are the coefficients of mobility expressed by M_X and c_0. Next, we will briefly review the important points of modified LBM theory.[21] At first, it is assumed that the system can be described by the functional $c(\mathbf{r})$ that is the composition at position $\mathbf{r}$ in real space, and a coarse-graining free energy written in the Ginzburg-Landau form:

$$F\{c(\mathbf{r})\} = \int [K(\nabla c)^2 + f(c)]d\mathbf{r}, \qquad (2.2)$$

where K is a gradient energy coefficient. The first term of the integrated function means the excess free energy due to the existence of composition gradient and the second term is the Helmholz free-energy density of the homogeneous system. Instead of the distribution of composition in real space, LBM theory[10] describes the state of system using the structure factor that is the Fourier transform of the spatial two-body correlation function on composition. The spatial two-body correlation function is

$$S(|\mathbf{r}-\mathbf{r}_0|) = \int u(\mathbf{r})u(\mathbf{r}_0)\rho(\{c\},t)\,\delta\{c\}. \qquad (2.3)$$

The time dependence of correlation function is defined from the change of probability distribution functional $\rho(\{c\},t)$ defined on the $c(\mathbf{r})$. Besides, the time dependence of $\rho(\{c\},t)$ obeys the master equation. Since available numerical techniques for solving the change of $\rho(\{c\},t)$ need a huge amount of calculation, the following approximation is made. If there is no correlation between probability distributions at two different points, it is possible to use the function $\rho(u,t)$ instead of the functional $\rho(\{c\},t)$. Moreover, it is considered that the probability distribution has two peaks when the phase decomposition sufficiently takes place. Hence LBM theory approximately uses the distribution function of the composition at an arbitrary position, which is a sum of displacement Gaussians:

$$\rho(u) = \frac{b_2}{\sqrt{2}\sigma(b_1+b_2)} \exp\left[-\frac{(u-b_1)^2}{2\sigma^2}\right]$$
$$+ \frac{b_1}{\sqrt{2}\sigma(b_1+b_2)} \exp\left[-\frac{(u+b_2)^2}{2\sigma^2}\right]. \qquad (2.4)$$

There remain three positive parameters b_1, b_2, and σ that mean two average values and standard deviation, respectively. After some mathematical operations using the above equations, finally, the present new mathematical result on the motion equation of structure factor is expressed by the following equations, which are called hereafter the modified LBM theory (MLBM):[21]

$$\frac{\partial\tilde{S}(\mathbf{k},t)}{\partial t} \cong 2k^2[2k^2\tilde{B}+\tilde{A}]\tilde{S}(\mathbf{k},t) + 2M_0k^2k_BT, \qquad (2.5)$$

$$\tilde{A} = \sum_{n=0}^{3} \bar{M}_n \sum_{m=2}^{\infty} \frac{m-1}{n+m-1} \frac{1}{(m-1)!} \frac{d^m f}{dc_0^m} \frac{\langle u^{n+m}\rangle}{\langle u^2\rangle}, \qquad (2.6)$$

$$\tilde{B} = \sum_{n=0}^{3} \bar{M}_n \frac{1}{n+1} \frac{\langle u^{n+2}\rangle}{\langle u^2\rangle}, \qquad (2.7)$$

where k_B is the Boltzmann constant. In formulating equations of MLBM theory, a few approximations were needed. (1) When the product of K and $\bar{M}$, and the other one of the free-energy density and $\bar{M}$ are expanded in a polynomial series about $\nabla^n u$ in the development of equations, we neglect some high-order terms for avoiding the difficulty. (2) In the second term of Eq. (2.5) as the effect of thermal fluctuation, we use a constant value $\bar{M}_0$ instead of the function $\bar{M}(u)$. The other equations in MLBM theory needed for calculation have essentially the same form as the ones of the original LBM theory in Ref. 10 except for the replacement of MA and MK with $\tilde{A}$ and $\tilde{B}$.

We will now consider the meaning of new nonlinear terms introduced by formulating MLBM theory. From the conceptual and physical viewpoint, while the original LBM theory considers the correlation about the gradient of chemical potential, the present MLBM theory considers the correlation of the flux of diffusion atom. The fact means that the formation of the structure depends on the tendency of not only the chemical potential, but also ''the flow'' of the chemical potential to become homogeneous. We can see the positive nonlinear effects as the result of expansion in Eqs. (2.6) and (2.7). The first summation of Eq. (2.6) and the summation of Eq. (2.7), if we neglect the terms in $n>0$, are the same as MA and MK in the original equations of LBM theory. On the other hand, from the approximately phenomenological viewpoint, $\tilde{A}$ is equivalent to the product of the mobility M and $(\partial^2 F/\partial c^2)_{c=c_0}$ in the Cahn's linear theory,[3] which is similar to the diffusion coefficient. In the states where $(\partial^2 F/\partial c^2)_{c=c_0}<0$ the diffusion coefficient is negative and the diffusion from the low composition area to the high composition area, which is called ''up-hill'' diffusion, occurs. Thus, the negative value of $\tilde{A}$ indicates a tendency of phase decomposition, and its absolute value gives the decomposition rate.

Next, we shall consider conditions when the nonlinear terms are effective. To formularize the MLBM theory, we used $\nabla M\nabla$ instead of $M\nabla^2$ in Eq. (2.5) in Ref. 10. Both terms are the same under these conditions:

$$(\bar{M}_1 + 2\bar{M}_2 u + 3\bar{M}_3 u^2)\nabla u = 0. \qquad (2.8)$$

If either the part parenthesized or ∇u is equal to 0, Eq. (2.8) is satisfied. The former condition is meaningless because it means that there is no dependence of the composition on mobility. As for the latter condition, ∇u is equivalent to the degree of the fluctuation of composition. The small fluctuation of composition makes ∇u nearly equal to 0. Thus, in the very early stage of phase decomposition, the latter condition is experimentally fulfilled. In other words, even if the phase decomposition progresses slightly, we have to use MLBM theory.

III. COMPUTER SIMULATION AND DISCUSSION

In order to investigate the effect of nonlinear terms on the phase decomposition, we carried out the calculation of time evolution of structure factor on the spinodal decomposition. In this paper, we tested a binary alloy system defined by the regular solution free energy in the case of $T_c=1000$ K. We

TABLE I. The parameters and condition used for the calculation.

Critical temperature	T_c (K)	1000
Interaction parameter	Ω (ergs/cm^3)	2.34×10^{10}
Gradient energy coefficient	K (ergs/cm)	3.85×10^{-5}
Lattice constant	a (Å)	2.87
Diffusion constant (A atom)		
	D_0 (cm^2/s)	398
	Q_0 (kJ/mol)	325
Mobility (A atom)	M_A (cm^5/ergs s)	
	(800 K)	2.76×10^{-19}
	(900 K)	5.63×10^{-17}
	(950 K)	5.26×10^{-16}
Temperature	T (K)	800, 900, 950
Composition	c_0	0.30, 0.45
Maximum wave number	k_{max} (Å^{-1})	1.57
Increment of wave number	Δk (Å^{-1})	5.0×10^3
Calculation time	$\tau (= 10^{-10} t M_0 / a^2)$	0–2000
Increment of time	$\Delta \tau$	1.0×10^{-5}

supported the realistic experiment as follows. The solute compositions c_0 are 0.3 and 0.45. After the solution treatment at 1273 K the sample is isothermally aged at 800, 900, and 950 K. Other thermodynamic parameters were fitted to the Fe-Cr binary alloy system.[22] The numerical values are given in Table I. The initial state after solution treatment was assumed by an Ornstein-Zernike (OZ) type structure factor.[4] The three parameters of $\rho(u,t)$ at $t=0$ were imposed suitable small values under conditions as follows. (1) $b_1 > 0$, $b_2 > 0$, and $\sigma > 0$. (2) $[b_1 b_2 \leqslant \langle u^2 \rangle]$. We used the normalized time defined by $\tau = 10^{-10} t (\bar{M}_0 / a^2)$. The calculation for $\tau = 2000$ is approximately equivalent to the realistic aging condition for 2 Ms in Fe-Cr alloy at 800 K, at which the phase decomposition experimentally progresses fully.[23]

The calculated results of time evolution of the structure factor as a function of wave number k are shown in Fig. 1. The conditions are (a) $c_0 = 0.45$ and $T = 800$ K and (b) $c_0 = 0.30$ and $T = 950$ K. The solid lines and the broken lines show the results of MLBM and LBM theory, respectively. At the very early stage, $\tilde{S}(k)$ is almost the initial OZ type. At $\tau = 2$, the $\tilde{S}(k)$ increases in the high-k region, and begins to show the peak. Then the peak increases and shifts to the smaller k with increasing time. The peak position k_m is supported to be inversely proportional to the wavelength of the periodic structure. Thus the decrease of k_m is consistent with the increase of wavelength of composition fluctuation. k_m due to MLBM theory is the slightly larger rather than one of LBM theory. According to the suggestions of experimental and theoretical results, the peak position k_m and the peak intensity I_m change according to the power law $\propto \tau^n$, and the present calculated results are no exception. The exponents n are shown in Table II. The exponents do not have a remarkable temperature dependence except for $c=0.3$ due to LBM theory, for which the value of n changes rapidly with the supersaturation. In Fig. 1(b), the peak obtained from MLBM theory increases rapidly and $\tilde{S}(k)$ becomes sharper than that from the original LBM theory. When the supersaturation is small in the case of Fig. 1(b), the difference between results
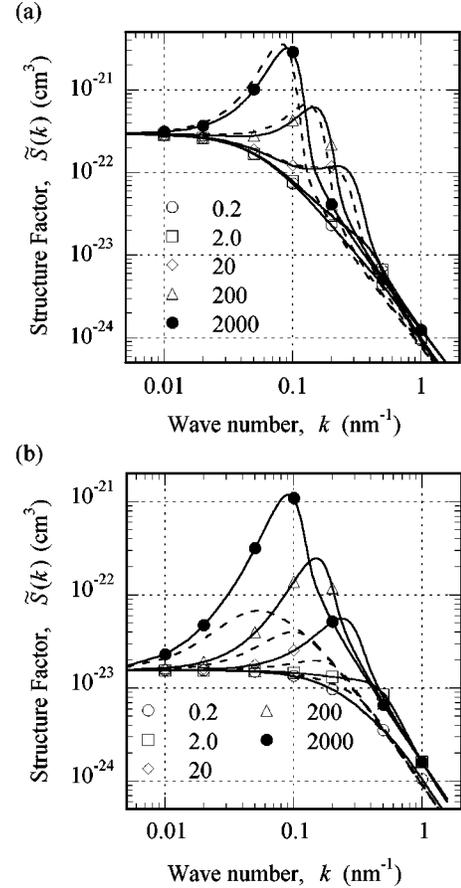

FIG. 1. The time development of the structure factor $\tilde{S}(k)$ calculated by modified LBM theory (MLBM) and LBM theory. The calculation conditions are (a) $T=800$ K, $c_0=0.45$ and (b) $T=950$ K, $c_0=0.30$. The solid and broken lines represent MLBM and LBM.

on both theories is enhanced. But there is not such a remarkable difference in Fig. 1(a) as the result with large supersaturation. The fact can be explained as follows. In the case of LBM theory, the tendency of phase decomposition mainly obeys the value of $(\partial^2 F / \partial c^2)_{c=c_0}$, of which absolute value decreases with decreasing the supersaturation. Therefore in Fig. 1(b), the change of structure factor due to LBM theory is moderate. On the other hand, in the case of the present MLBM theory the tendency of phase decomposition, we think, obeys the effects of the newly introduced nonlinear terms, and then they are not responsible to super-

TABLE II. Exponents n $(\propto \tau^n)$ obtained by the simulations based on the original LBM theory and the modified LBM theory.

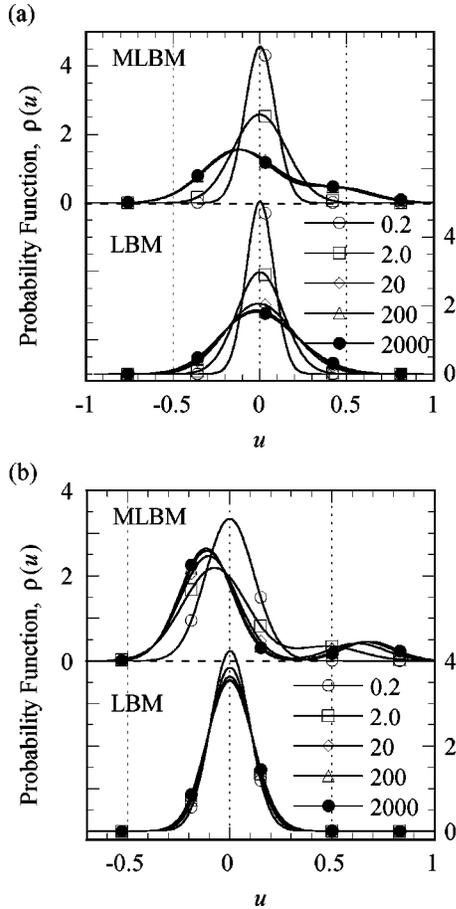| Composition	Temperature (K)	LBM k_m	MLBM k_m	LBM I_m	MLBM I_m
0.3	800	-0.189	-0.205	0.668	0.740
	900	-0.214	-0.205	0.436	0.694
	950	-0.252	-0.206	0.280	0.656
0.45	800	-0.198	-0.201	0.740	0.715
	900	-0.187	-0.197	0.734	0.708
	950	-0.177	-0.197	0.728	0.703

FIG. 2. The time development of the probability distribution function $\rho(u)$ calculated by modified LBM theory (MLBM) and the original LBM theory. The calculation conditions are (a) $T = 800$ K, $c_0 = 0.45$ and (b) $T = 950$ K, $c_0 = 0.30$. The solid and broken lines represent MLBM and LBM theory.

FIG. 3. The change of the values of $\widetilde{A}$ and $\widetilde{B}$ defined by Eqs. (2.6) and (2.7) as a function of calculation time τ calculated by modified LBM theory (MLBM) and LBM theory. (But, in the case of LBM MA and MK in Ref. 10 are used instead of $\widetilde{A}$ and $\widetilde{B}$, respectively.) The calculation conditions are (a) $T = 800$ K, $c_0 = 0.45$ and (b) $T = 950$ K, $c_0 = 0.30$. The solid and broken lines represent MLBM and LBM.

saturation. Therefore the change of structure factor due to MLBM theory does not have a prominent temperature dependence.

It is one of the characteristic points in these theories to evaluate the change of probability distribution function. The values of b_1 and b_2 in Eq. (2.4) are corresponding to the average composition the higher and the lower composition range of fluctuation structure and the differences of b_1 and b_2 are equivalent to its amplitude. The time evolution of the probability distribution function $\rho(u)$ is shown in Fig. 2. The composition dependence of $\rho(u)$ has a peak around the average composition $u = 0$ in the early stage. Continuously the peak becomes broader with increasing time. In Fig. 2(a), the shoulder appears in the high composition range at $\tau = 20$ in the case of MLBM theory. The shoulder gives an indication of the phase decomposition. As for Fig. 2(b) the peak of $\rho(u)$ splits into two peaks at $\tau = 2$, that means the phase decomposition is taking place in the same manner as shown in Fig. 2(a). Then, the small peak in the right-hand side shifts to the right and becomes shaper. Considering the result along with Fig. 1, it is found out that the growth of the amplitude of fluctuation occurs earlier than the formation of the characteristic periodic structure concerned with k_{m}. On the other hand, $\rho(u)$ of original LBM theory only becomes broader with increasing time and does not split. Moreover, the degree
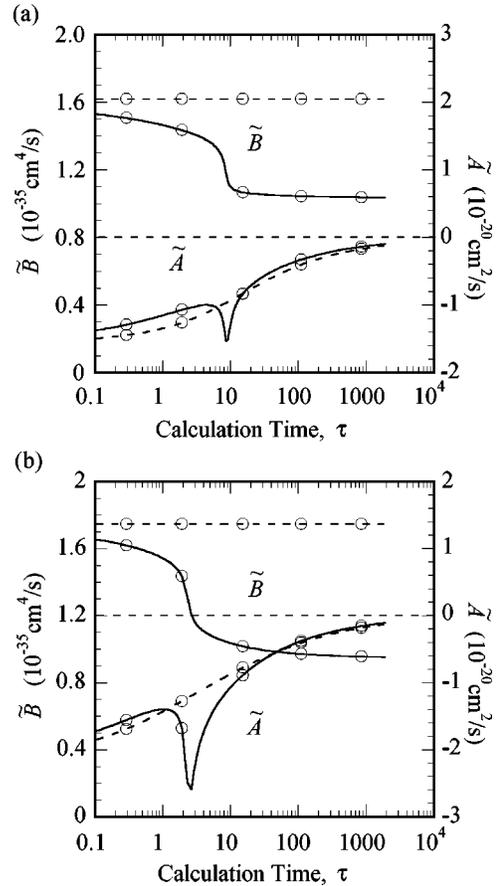
of change in Fig. 2(b) is weaker than the one in Fig. 2(a). As compared with the real Fe-Cr alloy aged for time equivalent to calculation time, we think that the result of the present modified theory fits with the experiment result[23] rather than the original one.

Here, the remarkable point is that the phase decomposition due to MLBM theory takes place rapidly in the early stage as a result of the effects of proposed nonlinear terms. The terms include the time-dependent higher order $\langle u^n \rangle$ linked with the change of $\rho(u)$ as in Fig. 2. The time dependence of the nonlinear terms $\widetilde{A}$ and $\widetilde{B}$ (which are corresponding to MA and MK in the case of LBM theory) is shown in Fig. 3. In the MLBM theory, the value of $\widetilde{A}$ makes a characteristic negative peak at around specific time while the value of $\widetilde{B}$ decreases. In the case of LBM theory, MA increases gradually with increasing time and MK keeps constant. The time-evolution process on MLBM theory can be divided into three stages in accordance with $\widetilde{A}$. In the first stage the difference between LBM and MLBM theory is trivial. In the second stage, $\widetilde{A}$ due to MLBM theory suddenly decreases, and $\rho(u)$ in Fig. 2 begins to split into two peaks. At the third stage, $\widetilde{A}$ turns to increase and becomes close to
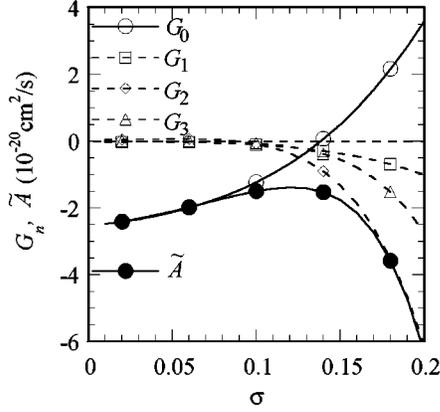
FIG. 4. The change of the nonlinear terms G_n ($n=0\sim3$) defined by Eq. (3.2) and $\widetilde{A}$ as a function of standard deviation σ. The calculation condition is as follows: $T=800$ K, $c_0=0.3$, $b_1=0.08$, and $b_2=0.02$.
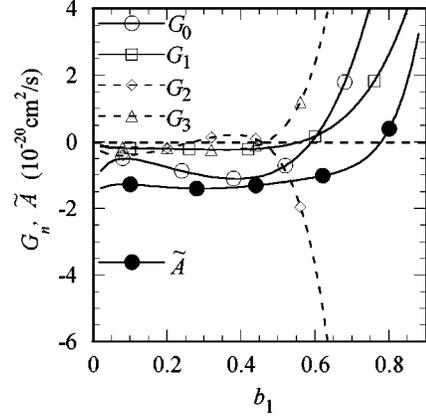

FIG. 5. The change of the nonlinear terms G_n ($n=0\sim3$) and $\widetilde{A}$ as a function of average composition in the range of high composition b_1. The calculation condition is as follows: $T=800$ K, $c_0=0.3$, $b_2=0.1$, and $\sigma=0.1$.

MA of LBM theory. On the whole, the degree of change in Fig. 3(b) is greater than the one Fig. 3(a) in agreement with the tendencies in Figs. 1 and 2. Since $\widetilde{A}$ is corresponding to the diffusion coefficient, the negative peak of $\widetilde{A}$ in the second stage predicts that the rate of phase decomposition become larger. Besides, $\widetilde{A}$ and $\widetilde{B}$ influence the periodic structure. The peak position k_m is also determined by $\widetilde{A}$ and $\widetilde{B}$. $\widetilde{S}(k)$ at $k_R=[-\widetilde{A}(t)/2\widetilde{B}(t)]^{1/2}$ increase more rapidly than the others do. The negative peak of $\widetilde{A}$ and the decrease of $\widetilde{B}$ in the second stage makes k_R larger. As a result, k_m due to the present MLBM theory is larger than in LBM theory as shown in Fig. 1.

Considering the discussion mentioned above, when the form of the probability distribution function is broad and unsymmetrical, the nonlinear terms become significant. In order to evaluate the relation between the introduced nonlinear terms and the system state defined as $\rho(u)$, Eq. (2.6) is divided as follows:

$$\widetilde{A}=G_0+G_1+G_2+G_3, \qquad (3.1)$$

$$G_n=\bar{M}_n\sum_{m=2}^{\infty}\frac{m-1}{n+m-1}\frac{1}{(m-1)!}\frac{d^m f}{dc_0^m}\frac{\langle u^{n+m}\rangle}{\langle u^2\rangle}. \quad (3.2)$$

Here, G_0 is the same as MA of LBM theory. The change of $\widetilde{A}$ and G_n is corresponding to the change of the function $\langle u^n\rangle$ linked with $\rho(u)$ defined by three parameters b_1, b_2, and σ. According to calculated results, $\rho(u)$ becomes broader from the first to the second stage, and thus the dependence of nonlinear terms as a function of σ is important. From the second to the third stage, $\rho(u)$ has the second peak, therefore the dependence of nonlinear terms as a function of b_1 is important. To investigate the relation of the nonlinear terms and $\rho(u)$ in detail, we calculated the change of nonlinear terms as a function of these parameters. In the real phase decomposition, the three parameters change at the same time. However, in order to understand clearly the roles of parameters, it is assumed that the other two parameters, except the one of interest, are constant. The calculated result of the σ dependence of $\widetilde{A}$ and G_n is described in Fig. 4. In

MLBM theory, $\widetilde{A}$ is a negative value and almost the same as G_0 in the range of small σ. With increasing σ, $\widetilde{A}$ turns to decrease as the change of G_2 though G_0 is continuously increasing into the positive value. The fact means that the broad $\rho(u)$ speeds up the phase decomposition in MLBM theory; on the other hand, the broad $\rho(u)$ reduced it in LBM theory as shown in Fig. 2. This fact explains the behavior of $\widetilde{A}$ in the second stage in Fig. 3. Next, the dependence of b_1 is shown in Fig. 5. In LBM theory, G_0, that is, MA, is negative in the range of small b_1 and turns into positive with increasing b_1. The value of b_1 at $G_0=0$ is roughly similar to the equilibrium composition given by free energy thermodynamically. In MLBM theory, at first G_2 and G_3 change dramatically. But the values almost cancel each other and just reduce $\widetilde{A}$ a little. Then $\widetilde{A}$ turns out to be more positive as G_1 changes at larger b_1 than the one of LBM theory. It is possible to explain the behavior of $\widetilde{A}$ in the third stage by Fig. 5. Here things to be emphasized among both results are that the phase decomposition is controlled by the present nonlinear terms in MLBM theory, but are not influenced by the degree of thermodynamical supersaturation as contrasted with the original LBM theory. Thus we have to regard the nonlinearity concerned with the composition dependence of mobility as important with regard to the phase decomposition process. From now on, we think, it is necessary to make clear the theoretical and phenomenological meanings of the nonlinear terms G_n.

IV. CONCLUSION

We extended the LBM theory considering the composition dependence of mobility. From the phenomenological point of view, the comparison of the calculation based on both theories made clear the following facts. In the case of the present MLBM theory, in spite of the small degree of the supersaturation the phase decomposition sufficiently takes place. And the amplitude of the composition fluctuation rapidly became large in the early stage. In the original LBM, the phase decomposition progressed gradually. Especially when the probability distribution function becomes broad, the phase decomposition in the present MLBM theory speeds up,

but in LBM theory it makes slow progress. The point emphasized by the authors is especially that these facts are caused by the introduced nonlinear terms controlling the phase decomposition.

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