Theoretical Study of Spinodal Decomposition at Intermediate Stages

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Theoretical study of spinodal decomposition at intermediate stages

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A computational method for the spinodal decomposition is presented on the basis of a nonlinear theory proposed by Langer, Bar-on, and Miller [Phys. Rev. A **11**, 1417 (1975)] (LBM) with an application of Suzuki's [Prog. Theor. Phys. **56**, 77 (1976); **56**, 477 (1976); **57**, 380 (1977); Adv. Chem. Phys. **46**, 195 (1981); J. Stat. Phys. **49**, 977 (1987)] general scaling theory for transient phenomena. The results were compared with experimental observations for a typical polymer-blend system with respect to the experimentally accessible quantities such as the structure factor and the single-point distribution function. The main features observed in scattering experiments were reproduced by this method. The inequality $\beta > 3\alpha$ was found in the numerical analyses when fitting the power-law relations expressed by $q_m \propto t^{-\alpha}$ and $S_m \propto t^{\beta}$ to the time variations of the dominant Fourier component of concentration fluctuations q_m and the corresponding structure factor S_m. It is shown that the LBM theory can be used to describe the phase-separation behavior up to intermediate stages.

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I. INTRODUCTION

The dynamics of ordering processes by spinodal decomposition has been the subject of many theoretical and experimental investigations in the field of small molecules concerning binary alloys, fluid mixtures, and inorganic glasses [1]. In recent years, such studies have also become popular in the field of polymer-blend systems [2]. This is due to the high viscosity of polymeric systems associated with the connectivity of monomers, which slows down the dynamics and enables us to probe the phase-separation behavior over wide time scales. According to experimental observations [3–5], the process of spinodal decompositions occurring in polymer blends can be qualitatively classified into three time regimes: (i) the early stage, where the spatial concentration fluctuations increase in amplitude while preserving the same wavelength; (ii) the intermediate stage, where both the amplitude and the wavelength increase with time; and (iii) the late stage, where the amplitude reaches the equilibrium value and only the wavelength grows with time.

For the early stage, the validity of the linear Cahn-Hilliard-Cook [6] theory has been examined with many experimental studies for polymer blends [7], and also with the Monte Carlo simulation method for the kinetic Ising model [8]. However, the theory does not account for intrinsically nonlinear effects in the later stages such as coarsening. There are several theoretical explanations of late-stage behavior such as the coarsening of domains with sharp interfaces [9], and the vaporization-condensation mechanism [10]. The domain growth in the late stage has been also studied by numerical [11] and Monte Carlo simulation methods [12]. The time dependence of the characteristic domain size was shown to satisfy a power law in the late stage. For polymeric systems [13], similar behavior was found in a detailed numerical study for three dimensions, starting from a full Flory–Higgins–de Gennes–type free energy and numerically integrating the time-evolution equation of the order parameter. These results are consistent with a modified Lifshitz-Slyozov law [14].

On the other hand, in the intermediate stage the nonlinear effects that are ignored in the Cahn-Hilliard-Cook theory are known to become important, and the time dependence of the characteristic quantities shows different behavior than in the early and late stages. Many theories have attempted to incorporate nonlinear effects into a theory of spinodal decomposition. Langer and coworkers [15,16] have presented successful theories to date. In particular, Langer, Bar-on, and Miller's [16] (LBM) theory quantitatively accounts for the nonlinear effects by assuming a form for the two-point distribution function. However, there exist some difficulties limiting the applicability of the LBM theory to the analysis of the dynamics of phase separation experiments. One of them is a cumbersome calculation for the moments of the order parameter. To solve a generalized diffusion equation in the theory, a sum of two Gaussians was chosen for a single-point distribution function under the assumption that the distribution of the order parameter in the intermediate stage can be considered as a double-peaked function. However, this assumption has no theoretical basis and the distribution cannot be precisely expressed by the sum of two Gaussian functions during spinodal decomposition. Another problem is that there remain a number of time-dependent parameters to be determined when the double Gaussian approximation is adopted. This involves solving a group of complicated moment equations iteratively.

In this paper we present a method for calculations based on LBM theory by applying a general scaling theory of transient phenomena proposed by Suzuki [17], and compare with experimental results for the phase separation of a typical polymer blend system at a real time scale. The quantities computed in this study are experimentally accessible, such as the structure factor and the single-point distribution function. Suzuki's scaling theory is based on a generalized scale transformation of time and is useful for the discussion of relaxations in nonequilibrium systems near an unstable point. Recently, this theory has been applied by Kawasaki, Yalabik, and Gunton [18] to a system with a nonconserved order parameter to study the growth of fluctuations in a quenched time-dependent Ginzburg-Landau (TDGL) model. We will show that the characteristic features observed in the intermediate stage can be reproduced with the LBM approximation scheme.

II. THEORETICAL BACKGROUND

We assume here that the coarse-grained free-energy functional $F[c]$ for a given concentration $c(r,t)$ has the Ginzburg-Landau form

$$F=\tfrac{1}{2}\int d^3r[f(c)+K|\nabla c(r)|^2] \tag{1a}$$

$$=\tfrac{1}{2}\int d^3r\left[-\gamma(c-c_0)^2+\frac{g}{2}(c-c_0)^4+K|\nabla c(r)|^2\right], \tag{1b}$$

where $f(c)$ is the free-energy density for a uniform system. We consider here a simple case that the free energy $f(c)$ is symmetrical about $c=c_0$, where c_0 is the average concentration, and has positive parameters γ and g denoting the instability and nonlinearity of a system, respectively. Recent works [11–13,19] have also shown that Eq. (1) is a satisfactory expression as the form of functional $F(c)$ for a description of spinodal decomposition that takes place in the unstable region. The last term of Eq. (1) represents a contribution from the concentration gradient with a coefficient K. Correspondingly, the final form of the LBM theory for the spinodal decomposition is represented by the following equation of motion for the structure factor $S(q,t)$ [16]:

$$\frac{\partial S(q,t)}{\partial t}=-2Mq^2\left[Kq^2+\left[\frac{\partial^2 f}{\partial c^2}\right]_{c=c_0}+\frac{1}{6}\left[\frac{\partial^4 f}{\partial c^4}\right]_{c=c_0}\frac{\langle u^4\rangle}{\langle u^2\rangle}\right]S(q,t)+(2MRT/V)q^2\ , \tag{2}$$

where M is mobility, q is the wave number, T is the temperature, V is the molar volume, and R is the gas constant. The order parameter u is related to concentration c through $u=c-c_0$. The quantities $(\partial^2 f/\partial c^2)_{c=c_0}$ and $(\partial^4 f/\partial c^4)_{c=c_0}$ correspond to the parameters γ and g in Eq. (1), respectively. Using the dimensionless variable X defined by

$$X\equiv u/u_s,\quad u_s=\left[-\frac{6(\partial^2 f/\partial c^2)_{c=c_0}}{(\partial^4 f/\partial c^4)_{c=c_0}}\right]^{1/2}, \tag{3}$$

Eq. (2) is reduced to

$$\frac{\partial S(q,t)}{\partial t}=-2Mq^2\left[Kq^2+\left[\frac{\partial^2 f}{\partial c^2}\right]_{c=c_0}\times\left[1-\frac{\langle X^4\rangle}{\langle X^2\rangle}\right]\right]S(q,t)+(2MRT/V)q^2\ . \tag{4}$$

In order to make further calculations, it is necessary to evaluate the time dependence of the terms $\langle X^4\rangle$ and $\langle X^2\rangle$. For argument on the relaxation and fluctuation in nonequilibrium systems near an unstable point, the recent work of Suzuki [17] on simple stochastic models with small nonlinear couplings seems particularly interesting. The results obtained from Suzuki's theory are considered to give an appropriate form of the distribution function required in the calculation based on the LBM theory, and the functional form will be easily determined once free-energy density is given.

The main idea of Suzuki's scaling theory [17] is to divide the whole range of time into three regions: (i) the initial region, in which linear approximation is valid; (ii) the scaling region, in which nonlinearity plays an essential role and the scaling law holds; and (iii) the final region, in which the system approaches the equilibrium state. The three regions can be considered to correspond qualitatively to the three stages of phase separation mentioned above at the beginning and there are no distinct boundaries between these time domains. More explicitly, we show the scaling theory in the following nonlinear Fokker-Planck equation:

$$\frac{\partial P(X,t)}{\partial t}=\left[-\frac{\partial}{\partial X}L(X)+\epsilon\frac{\partial^2}{\partial X^2}\right]P(X,t)\ , \tag{5}$$

where ϵ is the smallness parameter denoting the strength of random force. The first term on the right-hand side of Eq. (5) represents the drift part, while the second term represents the diffusion part. $L(X)$ can be obtained by $-df/dc$, in this case $L(X)=\gamma X-gX^3$. In the initial region, the nonlinearity of the system is not important (see Appendix), so that Eq. (5) can be linearized as

$$\frac{\partial P(X,t)}{\partial t}=\left[-\frac{\partial}{\partial X}(\gamma X)+\epsilon\frac{\partial^2}{\partial X^2}\right]P(X,t)\ . \tag{6}$$

If we assume that the initial distribution function has the Gaussian form $P(X,0)=(2\pi\epsilon\sigma_0)^{-1/2}\exp[-X^2(2\epsilon\sigma_0)^{-1}]$ with a variance σ_0, solution of Eq. (6) is obtained as

$$P_{\text{int}}(X,t)=\frac{1}{\sqrt{2\pi\epsilon\sigma(t)}}\exp\left[-\frac{X^2}{2\epsilon\sigma(t)}\right], \tag{7}$$

with $\sigma(t)=(\sigma_0+\sigma_1)\exp(2\gamma t)-\sigma_1$; $\sigma_1=1/(2\gamma)$. For large t in the initial region this solution has the following scaling form:

$$P_{\text{int}}^{(\text{sc})}(X,t)=\frac{1}{\sqrt{2\pi\tau}}\exp\left[-\frac{X^2}{2\tau}\right], \tag{8}$$

where $\tau=\epsilon(\sigma_0+\sigma_1)\exp(2\gamma t)$.

In the scaling region, the diffusion term in Eq. (5) can be neglected asymptotically (see Appendix), so that Eq. (5) is reduced to the following simplified equation in a scaling form:

$$\frac{\partial}{\partial \tau}P_{\mathrm{sc}}+\frac{\partial}{\partial X}L(X)P_{\mathrm{sc}}=0 \ . \tag{9}$$

Equation (9) can be solved rigorously. One of the main features of the scaling theory is that it enables a determination of a general solution for Eq. (9), so that it may be connected smoothly with the dominant scaling solution [Eq. (8)] in the initial region. Thus the following scaling solution was obtained:

$$\begin{aligned} P(X,t) &\simeq P_{\mathrm{sc}}(X,t) \\ &= \frac{1}{\sqrt{2\pi\tau}}\exp\left[-\frac{H^2(X)}{2\tau}+\ln H'(x)\right] \\ &= \frac{1}{\sqrt{2\pi\tau}}\left[1-\frac{g}{\gamma}X^2(1-e^{-2\gamma t})\right]^{-3/2} \\ &\quad \times\exp\left[-\frac{X^2}{2\tau[1-(g/\gamma)X^2(1-e^{-2\gamma t})]}\right] , \end{aligned} \tag{10}$$

where $H(X)$ is defined by

$$H(X)=\exp\left[\int_{a_0}^{x}\gamma\Big/L(y)dy\right] .$$

The value of a_0 is determined so as to satisfy $H'(0)=1$.

III. RESULTS AND DISCUSSION

In order to examine the new computational method, we have performed numerical studies and have compared the computed results with the phase-separation experiments on the well-investigated polystyrene (PS) and poly (vinyl methyl ether) (PVME) blend. For the system studied by Hashimoto *et al.* [3,4], apparent diffusivity D_{app}, dominant wave number at $t=0$ $q_m(0)$, and $(\partial^2 f/\partial c^2)_{c=c_0}$ are known. The experiments were carried out on the critical composition (80% PVME by volume) with a temperature jump from 65 to 98.2 °C. For this composition the blend has a spinodal temperature $T_s=95.8$ °C. Using these quantities, the mobility M and the coefficient of concentration gradient K can be determined by $M=-D_{\mathrm{app}}/(\partial^2 f/\partial c^2)_{c=c_0}$ and $K=-(\partial^2 f/\partial c^2)_{c=c_0}/[4q_m(0)]$. Consequently, the values of M, K, and $(\partial^2 f/\partial c^2)_{c=c_0}$ at a given temperature are used as the input for the numerical studies.

Figure 1 shows the time variation of the quantity $1-\langle X^4\rangle/\langle X^2\rangle$ computed from Eq. (10). Since the ratio of g/γ is essential in the use of Suzuki's scaling theory [17], we have taken $g/\gamma=1$ to emphasize the importance of nonlinear effects, and chose the values of γ and ϵ in such a way that the time region in which $1-\langle X^4\rangle/\langle X^2\rangle$ rapidly reduces from almost 1 to 0.3 was taken to meet the intermediate stage (from 10 to 40 min). With the present computational method, the quantity $1-\langle X^4\rangle/\langle X^2\rangle$ deviated significantly from 1, showing a contrast with the linearized Cahn-Hilliard-Cook theory in which its value is essentially equal to 1.

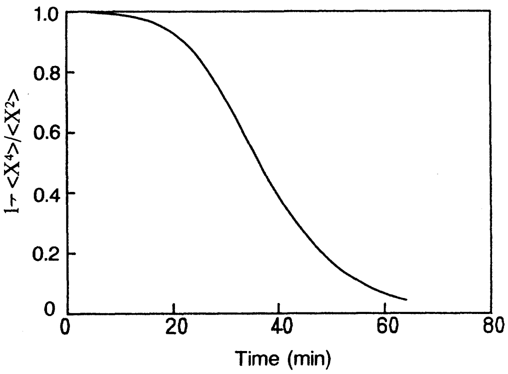

FIG. 1. The time variation of the quantity $1-\langle X^4\rangle/\langle X^2\rangle$ computed for $\gamma=g=0.1$ and $\epsilon=5\times10^{-5}$.

In Fig. 2 we show the time evolution of the structure factor computed from Eq. (4). The general trend observed from experiments in the intermediate stage (see Fig 4(c) in Ref. [3]) is reproduced in this figure: the maximum appears in the structure factor after the onset of spinodal decomposition, the structure factor maximum S_m increases and the dominant wave number q_m shifts toward smaller values with lapse of time. It is found in our numerical studies that the value of $q_m(0)$ which is related to parameter K strongly affects the peak position of the computed profiles. The values of $q_m(0)$ obtained from the analyses of early-stage data based on the linearized theory are generally much larger than those from the extrapolation of the observed q_m at $t=0$. We have used the extrapolated value for $q_m(0)$ in the present study for fitting experimental scattering intensity. This was found to give a better agreement with experiments.

It is well known that nonlinear growth from the inter-

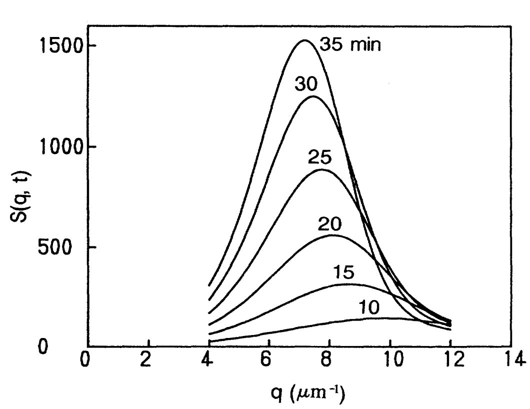

FIG. 2. The time evolution of the structure factor $S(q,t)$ computed from Eq. (4) for the intermediate stage of phase separation.

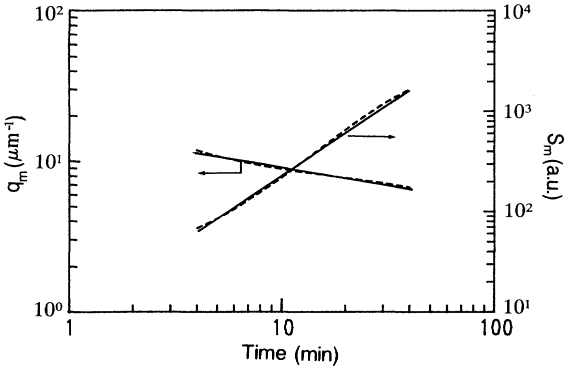

FIG. 3. The log-log plots of the computed dominant wave number q_m and the corresponding structure factor S_m against time (dashed lines). The straight lines are the best fits to the data, giving the values of 0.223 for α and 1.45 for β.

mediate stage can be better explained in terms of the time evolution of q_m and S_m by power laws $q_m(t) \propto t^{-\alpha}$ and $S_m(t) \propto t^{\beta}$, where the exponents α and β are used as a measure to characterize the proceeding of phase separation. Figure 3 shows the calculated evolutions of q_m and S_m corresponding to the result of Fig. 2. The power-law relations are shown to be approximately satisfied for both of the quantities over a time range from 5 to 50 min. The values of exponents α and β are found to be 0.223 and 1.45, respectively. By varying the values of quantities such as M, K, and $(\partial^2 f/\partial c^2)_{c=c_0}$, we obtained the exponents α in a range from 0.16 to 0.23 and β from1.2 to 3.1, satisfying the inequality $\beta > 3\alpha$. The values of α obtained in this study are in good agreement with those observed experimentally [4] and that predicted by the LBM theory [16], but smaller than those predicted by the Binder-Stauffer [9] and Lifshitz-Slyozov [10] theories for the late stage. This confirms that our computed results describe well the behavior of the phase separation occurring in the intermediate stage.

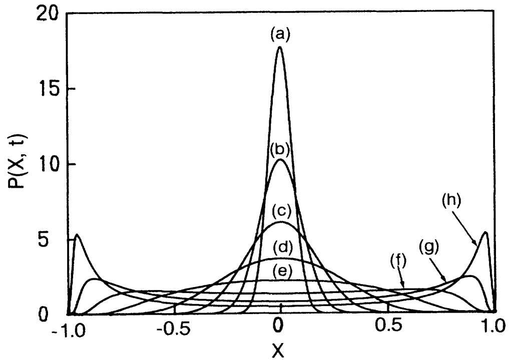

FIG. 4. The temporal evolution of the single-point distribution function $P(X,t)$ based on Suzuki's scaling theory with $\gamma = g = 0.1$ and $\epsilon = 5 \times 10^{-5}$. (a) $t = 10$ min ($\tau = 3.2 \times 10^{-3}$), (b) $t = 15$ min ($\tau = 9.5 \times 10^{-3}$), (c) $t = 20$ min ($\tau = 0.027$), (d) $t = 25$ min ($\tau = 0.074$), (e) $t = 30$ min ($\tau = 0.20$), (f) $t = 35$ min ($\tau = 0.55$), (g) $t = 40$ min ($\tau = 1.5$), (h) $t = 45$ min ($\tau = 4.0$).

Figure 4 shows the temporal evolution of the distribution function calculated by Eq. (10). $P(X,t)$ starts with a Gaussian function centered at $X = 0$, then broadens and eventually develops into two symmetrical peaks that rapidly separate from one another. The symmetry of $P(X,t)$ is attributable to the symmetric form of the free-energy density $f(c)$ in Eq. (1). Onset time t_0 is defined by the time at which the double peaks just begin to appear, and this is indicated by curve (f) in Fig. 4. The two macrophases are expected to form after t_0. The profiles of $P(X,t)$ are consistent with those obtained experimentally from digital imaging analysis for a PS-PVME blend by Tanaka and Nishi [20] and that from the computer simulation of the TDGL equation by Petschek and Metiu [19].

IV. CONCLUSIONS

In summary, we have shown a simplified computational method that combines the LBM theory with Suzuki's general scaling theory. The main features observed from scattering experiments of phase separation were reproduced by the present method. The values of the exponents for the power laws indicate that the computed results only describe the behavior of the intermediate stage of spinodal decomposition where the concentration fluctuations have not yet reached equilibrium state. By applying Suzuki's theory, the single-point distribution function can be evaluated theoretically from the nonlinear Fokker-Planck equation, and the computed results are in good agreement with those obtained from scattering and digital imaging analysis experiments and from computer simulations of the TDGL equation.

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APPENDIX

Here we report the brief separation procedure described in Suzuki's scaling theory. As mentioned in the text, the time region is divided into three regimes: (i) initial or linear regime; (ii) nonlinear, drift or scaling regime; and (iii) final regime.

If $x(t)$ is an intensive macrovariable defined by

$$x(t) = X(t)/\Omega \ , \tag{A1}$$

where Ω is the system size, we can separate it into two parts as

$$x(t) = y(t) + z(t) \ , \tag{A2}$$

where $y(t)$ denotes the most probable path of $x(t)$, and $z(t)$ is the remaining fluctuating part. Then the above three regimes (i)–(iii) are classified as follows:

$$z(t)=\begin{cases}O(\Omega^{-1/2}) & \text{in the initial regime}\\ O(1) & \text{in the scaling regime}\\ O(\Omega^{-1/2}) & \text{in the final regime}\ .\end{cases}$$

That is, the fluctuating part $z(t)$ differs in scaling behavior with respect to the system size in each regime when the system starts from (or near) the unstable point. This will be the simplest criterion for the classification of the above three regimes.

In the initial regime, the intrinsic fluctuation is very small (of order Ω) for a large Ω, and consequently a random force acting on the system plays an essential role in this regime. Otherwise, the system does not change its state under the unstable equilibrium initial condition. Furthermore, the nonlinearity of the system is not important in this regime because the deviation of $x(t)$ from the unstable point is small. Therefore, the temporal evolution of $x(t)$ in this initial regime is Gaussian and its distribution function satisfies the linear Fokker-Planck equation expressed by Eq. (6) in the text.

The fluctuating part $z(t)$ of Eq. (7) in the text is given by

$$z(t)\propto[\epsilon\sigma(t)]^{1/2} \text{ or } \sigma(t)\propto\epsilon^{-1}z^2(t)\ , \tag{A3}$$

and it becomes larger and larger as the time increases, although it is of order $\Omega^{-1/2}$ for a small t. When t increases to the order

$$t\simeq t_1\equiv(2\gamma)^{-1}\ln[\Omega/(\sigma_0+\sigma_1)] \tag{A4}$$

the fluctuating part $z(t)$ becomes of order unity [i.e., $z(t)\sim O(1)$], and thus the system is in the scaling regime for $t\sim t_1$. Namely, the linear, Gaussian approximation breaks down in the time regime. However, the Gaussian approximation predicts qualitatively what happens in the scaling regime. In fact, it shows that the fluctuation (or variance) is anomalously enchanced up to order unity (or $\Omega\equiv\epsilon^{-1}$) in the scaling regime. Note that this anomalous fluctuation of order unity is maximum from the definition of the fluctuation [cf. the fluctuation $\langle x^2\rangle_c=\langle x^2\rangle-\langle x\rangle^2\le\langle x^2\rangle\le(\text{maximum value of } x)^2=O(1)$]. Thus, the scaling behavior of $z(t)$ in the scaling regime is concluded to be $z(t)=O(1)$. This will be used effectively in the non-Gaussian scaling regime.

In the scaling regime, the fluctuating part $z(t)$ becomes of order unity, namely it satisfies the scaling property

$$z(t)\simeq O(1) \tag{A5}$$

(i.e., invariant for scaling of the size). This indicates that the distribution function is very broad and consequently that the diffusion effect is neglected effectively for a large system size Ω. Therefore, the distribution of x is governed asymptotically by the drift equation in the scaling regime. More explicitly, the following Kramers-Moyal equation was discussed in Suzuki's theory:

$$\epsilon\frac{\partial P(x,t)}{\partial t}=-\mathcal{H}\left[x,\epsilon\frac{\partial}{\partial x}\right]P(x,t)\ , \tag{A6}$$

where

$$\mathcal{H}(x,p)=\int(1-e^{-rp})w(x,r)dr=\sum_n\frac{(-1)^{n-1}}{n!}p^n c_n(x) \tag{A7}$$

and

$$c_n(x)=\int r^n w(x,r)dr\ , \tag{A8}$$

with the transition probability $w(x,r)$. Assuming that all $c_n(x)$ are of order unity as usual, the scaling property of the nth term of the right-hand side of Eq. (A6) is of order Ω^{-n+1} in the scaling regime because all derivatives of $P(x,t)$ with respect to x are of order unity from the scaling property. Thus the first drift term is dominant in the scaling regime. That is, $P(x,t)$ satisfies asymptotically the following drift equation, which has the same form as Eq. (9) in the text:

$$\frac{\partial}{\partial t}P(x,t)+\frac{\partial}{\partial x}c_1(x)P(x,t)=0\ . \tag{A9}$$

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