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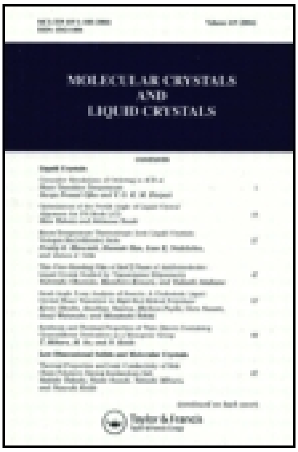

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Foundations and Extensions of the Cahn-Hilliard-Cook Theory

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Foundations and Extensions of the Cahn-Hilliard-Cook Theory†

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INTRODUCTION

In this paper we examine the foundations of the Cahn-Hilliard-Cook (CHC) theory of phase separation, which has been used routinely in recent years to interpret dynamic scattering experiments on binary polymer blends, and discuss its extension to multi-component mixtures. The CHC-theory is based on the following nonlinear Langevin equation[1]:

$$\frac{\partial\phi\,(\mathbf{q},t)}{\partial t} = -\beta\lambda(q)\,\mu(\mathbf{q}) + \eta(\mathbf{q},t), \tag{1}$$

where $\phi(\mathbf{q},t)$ is the Fourier transform of the local volume fraction $\phi(\mathbf{r},t)$ of one of the components of the binary mixture which is assumed to be incompressible; $\lambda(q)$ is the q-dependent onsager coefficient; $\mu(\mathbf{q},t)$ is the Fourier transform of the local chemical potential difference $\mu(\mathbf{r},t)$; and $\eta(\mathbf{q},t)$ is the random force which is added to account for the thermal fluctuations. The latter is assumed to be a stationary white noise process with zero mean and an autocovariance $\langle\eta(\mathbf{q},t)\,\eta(-\mathbf{q},t')\rangle = \lambda(q)\,q^2\,\delta(t-t')$, which is determined from fluctuation-dissipation theorem. The use of the Langevin equation method to describe fluctuations in nonlinear macroscopic systems, in the way done in the CHC theory, was questioned by van Kampen[2,3] for reasons which we discuss in this paper. The proper way of using the Langevin equation method in nonlinear systems was provided by Akcasu[4] in 1977 through van Kampen's system size expansion, which we sketch next.

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DERIVATION OF THE LANGEVIN EQUATION[4]

We select a set of extensive macrovariables $A_j(t)$, $j = 1, 2, \ldots$, which are considered to describe in sufficient detail a macrostate of the physical system under consideration. The number of particles of a given kind in a microscopically large cell in configuration space is an example of a macrovariable. One assumes that the fluctuations in these variables can be treated as a Markov process. One further assumes that the transition probability per unit time, $W(\mathbf{A},\mathbf{r})$, from $\mathbf{A}$ to $\mathbf{A} + \mathbf{r}$, of this random process is proportional to the size of the system Ω; i.e.,

$$W(\mathbf{A}, \mathbf{r}) = \Omega\, \omega(\mathbf{a},\mathbf{r}), \tag{2}$$

where $a_j(t) = A_j(t)/\Omega$ (the intensive variables), and $\omega(\mathbf{a}, \mathbf{r})$ is the intensive transition probability per unit time. Using only the Markov property, one obtains the following nonlinear Langevin equation for the realizations of $\mathbf{a}(t)$:

$$\mathbf{a}(t) = \mathbf{C}_1[\mathbf{a}\,(t)] + \mathbf{f}(t) \tag{3}$$

with

$$\begin{aligned} \langle \mathbf{f}(t)\rangle &= 0, \\ \langle \mathbf{f}(t)\, \mathbf{a}^+(0)\rangle &= 0 \quad (t > 0), \text{ and} \\ \langle \mathbf{f}(t)\, (\mathbf{f})^+(t')\rangle &= \langle \mathbf{C}_2[\mathbf{a}(t)]\rangle\, \delta(t - t'), \end{aligned} \tag{4}$$

where $\mathbf{x}^+$ denotes the transpose of the vector $\mathbf{x}$ (or hermitian conjugates, if components of $\mathbf{x}$ are complex). The vector $\mathbf{C}_1$ and the square matrix $\mathbf{C}_2$ are defined by

$$\begin{aligned} \mathbf{C}_1(\mathbf{a}) &\equiv \int d\,\mathbf{r}\;\mathbf{r}\;\omega(\mathbf{a}),\,(\mathbf{r}) \text{ and} \\ \mathbf{C}_2(\mathbf{a}) &\equiv \int d\,\mathbf{r}\;\mathbf{r}\;\mathbf{r}^+\omega(\mathbf{a}, \mathbf{r}), \end{aligned} \tag{5}$$

which are nonlinear functions of their vector arguments. It is observed that the autocovariance matrix of the random force, $\langle \mathbf{C}_2[\mathbf{a}(t)]\rangle$, involves all the yet unknown moments of $\mathbf{a}$, which one hopes to calculate using the Langevin equation. It is this dependence of the magnitude of random force on the unknown higher moments of $\mathbf{a}$, which makes the application of the Langevin equation method to nonlinear systems less straightforward, if not impossible, as pointed out by van Kampen.[3] One could, of course, replace $\langle \mathbf{C}_2[\mathbf{a}(t)]\rangle$ by a constant matrix as a "postulate" to obtain a "theory" of fluctuations in nonlinear systems, as it is done in CHC theory, and try to demonstrate its validity by comparing the theoretical predictions to experimental results. But such an ad-hoc procedure would be without foundation. Fortunately, it is possible to proceed more systematically[4] by resorting to a system-size expansion in which $\varepsilon = 1/\Omega$ is used as a smallness parameter. One first separates the mean $\langle \mathbf{a}(t)\rangle$ and the fluctuations about the mean $\boldsymbol{\xi}(t)$ as $\mathbf{a}(t) = \langle \mathbf{a}(t)\rangle + \varepsilon^{1/2}\, \boldsymbol{\xi}(t)$. The fluctuations are assumed to be of order $\varepsilon^{1/2}$ when the mean is of order

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ε^o. One then expands both $\langle \mathbf{a}(t) \rangle$ and $\boldsymbol{\xi}(t)$ in powers of ε as $\langle \mathbf{a}(t) \rangle = \mathbf{a}_0(t) + \varepsilon \mathbf{a}_1(t) + \ldots$, and $\boldsymbol{\xi}(t) = \boldsymbol{\xi}_0(t) + \varepsilon^{1/2}\, \boldsymbol{\xi}_1 + \ldots$ In the lowest order in ε, one obtains the following set of equations for $\mathbf{a}_0(t)$ and $\boldsymbol{\xi}_0(t)$:

$$\dot{\mathbf{a}}_0(t) = \mathbf{C}_1[\mathbf{a}_0(t)] \text{ and} \tag{6a}$$

$$\boldsymbol{\xi}_0(t) + \mathbf{R}[\mathbf{a}_0(t)]\, \boldsymbol{\xi}_0(t) = \mathbf{f}_0(t) \tag{6b}$$

where the square matrix $\mathbf{R}(\mathbf{a})$ is the gradient of $\mathbf{C}_1(\mathbf{a})$

$$\mathbf{R}(\mathbf{a}) = -\partial \mathbf{C}_1(\mathbf{a})/\partial\, \mathbf{a}, \tag{6c}$$

and $\mathbf{f}_0(t)$ is a random force with the following statistical properties:

$$\langle \mathbf{f}_0(t) \rangle = 0; \tag{7a}$$

$$\langle \mathbf{f}_0(t)\, \xi_o^+(t') \rangle = 0, \quad t > t'; \tag{7b}$$

$$\langle \mathbf{f}_0(t)\, \xi_o^+(t') \rangle + \langle \boldsymbol{\xi}_0(t)\, \mathbf{f}_o^+(t) \rangle = \mathbf{C}_2[\mathbf{a}_0(t)]; \text{ and} \tag{7c}$$

$$\langle \mathbf{f}_0(t)\, \mathbf{f}_o^+(t') \rangle \;\; \mathbf{C}_2[\mathbf{a}_0(t)]\, \delta(t - t'). \tag{7d}$$

The Equation (6a) is a deterministic equation and governs the time-dependence of $\mathbf{a}_0(t)$, which can be shown[5] to be the "most probable path" for the state vector $\mathbf{a}(t)$. It is also the mean in the lowest order in the inverse system size. The fluctuations about the mean satisfy Equation (6b), which is a "linear Langevin equation" with time-dependent coefficients. The autocovariance matrix of the random force, $\mathbf{C}_2[\mathbf{a}_0(t)]$ in Equation (7d), depends only on $\mathbf{a}_0(t)$, which is determined from the deterministic equation. Because the time dependences of $\mathbf{R}(t) \equiv \mathbf{R}[\mathbf{a}_0(t)]$ and $\mathbf{C}_2(t) \equiv \mathbf{C}_2[\mathbf{a}_0(t)]$ are implicit in $\mathbf{a}_0(t)$, we may say that in nonlinear systems the fluctuations are "driven" by the mean.

Equations (6) and (7) provide a systematic computational framework to study the fluctuations of macrovariables in nonlinear systems, either during transients following an initial perturbation or around an equilibrium state. The separation of the time evolution of the mean and fluctuations about the mean is the main difference between the above description and the nonlinear Langevin equation method used in the CHC theory.

CALCULATION OF CORRELATIONS

The dynamic structure factor $\mathbf{S}_D(t, t_o) = \langle \boldsymbol{\xi}_0(t)\, \boldsymbol{\xi}_0^+(t_o) \rangle$, which during transients depend on both t_o and t, immediately follows from Equations (6b) and (7b) as the following:

$$\mathbf{S}_D(t, t_o) = \mathbf{L}(t, t_o)\, \sigma(t_o), \quad t > t_o, \tag{8}$$

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where $\mathbf{L}(t, t_o)$ is the solution of

$$\frac{d}{dt}\mathbf{L}(t, t_o) = -\mathbf{R}(t)\mathbf{L}(t, t_o)$$

with $\mathbf{L}(t_o, t_o) = \mathbf{I}$. The variance $\boldsymbol{\sigma}(t) = \langle \boldsymbol{\xi}_o(t)\, \boldsymbol{\xi}_o^+(t)\rangle$ satisfies

$$\dot{\boldsymbol{\sigma}}(t_o) + \mathbf{R}(t)\,\boldsymbol{\sigma}(t) + \boldsymbol{\sigma}(t)\,\mathbf{R}^+(t) = \mathbf{C}_2(t), \tag{9}$$

which is obtained from Equations (6b) and (7c). This equation can be solved in terms of the transition matrix $\mathbf{L}(t, t_o)$ as

$$\boldsymbol{\sigma}(t) = \mathbf{L}(t, t_o)\,\boldsymbol{\sigma}(t_o)\,\mathbf{L}^+(t, t_o) + \int_{t_o}^{t} du\,\mathbf{L}(t, t')\,\mathbf{C}_2(t')\,\mathbf{L}^+(t, t'). \tag{10}$$

It is noted that the matrix $\mathbf{L}(t, t_o)$ can be interpreted as the "normalized dynamic structure factor."

CONNECTION WITH THE LINEAR CAHN-HILLIARD-COOK THEORY

The equilibrium states of the nonlinear system are determined from $C_1(\mathbf{a}_e) = 0$. An equilibrium state is stable if $\mathbf{R} \equiv \mathbf{R}(\mathbf{a}_e)$ is positive definite, and unstable otherwise. We can "linearize" the deterministic Equation 6a about $\mathbf{a}_e$ as $\delta\mathbf{a}_o(t) \cong -\mathbf{R}\,\delta\mathbf{a}_o(t)$, where $\delta\mathbf{a}_o(t)$ denotes the deviations of the mean from its equilibrium value. The solution is expressed in terms of $\mathbf{L}(t) \equiv \mathbf{L}(t, o) = \exp[-\mathbf{R}t]$ as $\delta\dot{\mathbf{a}}_o(t) = \mathbf{L}(t)\,\delta\mathbf{a}_o(t)$. Because it is already linear, there is no need to linearize the Langevin equation to proceed further. One may still allow $\mathbf{C}_2[\mathbf{a}_e + \delta\mathbf{a}_o(t)]$ in Equations (7) and (9), to depend on $\delta\mathbf{a}_o(t)$ for a more precise description. However, it is not inconsistent with the linearization procedure to ignore $\delta\mathbf{a}_o(t)$ in the argument and replace $\mathbf{C}_2[\mathbf{a}_o(t)]$ by $\mathbf{C}_2 \equiv \mathbf{C}_2\,(\mathbf{a}_e)$ in these equations. Then Equation (9) becomes

$$\dot{\boldsymbol{\sigma}}(t) + \mathbf{R}\,\boldsymbol{\sigma}(t) + \mathbf{R}^+\,\boldsymbol{\sigma}(t) = \mathbf{C}_2. \tag{11}$$

In a scattering experiment, in which the scattered intensity is measured as a function of time, one needs an equation for the one-time correlation function:

$$\mathbf{S}(t) \equiv \delta\,\mathbf{a}_o(t)\,\delta\mathbf{a}_o^+\,(t)\,\boldsymbol{\sigma}(t). \tag{12}$$

The time evolution of $\mathbf{S}(t)$ can be obtained from Equations (10) and (11); then using the expression of $\delta\,\mathbf{a}_o(t)$ given above, we find:

$$\mathbf{S}(t) = \mathbf{L}(t)\,\mathbf{S}_{\text{in}}\,\mathbf{L}^+\,(t) + \int_{o}^{t} ds\,\mathbf{L}(s)\,\mathbf{C}_2\,\mathbf{L}^+\,(s). \tag{13}$$

This is the extended form of the linear Cahn-Hilliard-Cook theory we mentioned

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earlier. $\mathbf{S}_{\text{in}}$ is the initial value of $\mathbf{S}(t)$. We can cast Equation (13) into a more familiar form by introducing $\mathbf{S}_{\text{eq}}$ through

$$\mathbf{C}_2 = \mathbf{R}\,\mathbf{S}_{\text{eq}} + \mathbf{S}_{\text{eq}}\,\mathbf{R}^+ \tag{14}$$

and using some identities, as

$$\mathbf{S}(t) = \mathbf{S}_{\text{eq}} + \mathbf{L}(t)\,[\mathbf{S}_{\text{in}} - \mathbf{S}_{\text{eq}}]\,\mathbf{L}^+\,(t). \tag{15}$$

The matrix $\mathbf{S}_{\text{eq}}$ introduced in Equation (14) is the static structure factor in the final equilibrium state when $\mathbf{R}$ is positive definite (stable equilibrium), because in this case $\sigma(t)$ in Equation (11) approaches asymptotically to $\mathbf{S}_{\text{eq}}$. However, one can still use Equation (14) to obtain the form in Equation (15), even when $\mathbf{R}$ is negative definite (unstable equilibrium). In this case $\mathbf{S}_{\text{eq}}$ is nonphysical and is usually referred to as the "virtual structure factor." In the case of stable equilibrium, Equation (14) represents the generalized Einstein relation, which is a kind of fluctuation-dissipation theorem.

CONNECTION WITH THE RANDOM PHASE APPROXIMATION

Calculation of $\mathbf{S}(t)$ from Equation (13) or (14) requires the knowledge of the relaxation (or growth) matrix $\mathbf{R}$ and the autocovariance matrix $\mathbf{C}_2$ as two inputs in the theory. They can be calculated as the first two moments of the transition probability per unit time $\omega(\mathbf{a}, \mathbf{r})$, if the latter can be obtained from the physical description of the system. In spatially inhomogeneous systems, this can be done by dividing the volume into cells and using discretized formulation of the diffusion process. They can also be determined using static and dynamic Random Phase Approximation (RPA). To illustrate this point, we consider an incompressible binary mixture of two polymer species and choose state vector $\mathbf{a}$ as the Fourier component of the incremental volume fraction of one of the components, i.e., $\mathbf{a} \rightarrow \delta\phi(\mathbf{q}, t)$. In this one component description, Equation (13) reduces to

$$S(q, t) = S_{\text{in}}(q)\,L^2(q, t) + C_2(q)\int_o^t du\,L^2(q, u), \tag{16}$$

where the relaxation function $L(q, t) = \exp[-R(q)t]$. In the Markov description, $L(q, t)$ is related to the linear response function $\chi(q, t)$ by

$$L(q, t) = \chi(q, t)/\chi(q, o),$$

because $\chi(q, t)$ is also exponential in the Markov limit. In RPA, the response function can be expressed in Laplace domain in terms of the mean response functions of the non-interacting components[6]

$$\chi^{-1}(q, s) = \chi_A^{-1}(q, s) + \chi_B^{-1}(q, s) - 2k_BT\chi_F,$$

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where the symbols have their conventional meanings. As discussed in Reference 6, these relations are valid both in the miscible (stable equilibrium) and in the spinodal regions (unstable equilibrium). Because non-interacting components are always stable, we can use the linear response theory to express $\chi_A(q, t)$ in terms of the equilibrium dynamic scattering function $S_A(q, t)$:

$$k_B T\chi_A\,(q, t) = -\phi_A \frac{d}{dt} S_A(q, t),$$

Hence, the calculation of $L(q, t)$ is reduced to the calculation of $S_A(q, t)$. The latter has been taken in the literature[1,7,8] as the single-chain dynamic scattering function, which is calculable exactly in Rouse dynamics.

We now return to the calculation of $C_2(q)$. In the miscible region, $C_2(q)$ can be expressed in terms of the static structure factor $S_{eq}(q)$ in the final equilibrium state using Einstein's relation (Equation (14)), which, in one component description, reduces to $C_2(q) = 2R(q)S_{eq}(q)$. The $S_{eq}(q)$ is calculable in RPA from DeGenne's formula

$$S_{eq}^{-1}(q) = [\phi_A\, S_{eq}^{A}(q)]^{-1} + [\phi_B\, S_{eq}^{B}(q)]^{-1} - 2\chi_F, \tag{17}$$

where $S_{eq}^{A}(q)$ is the static structure factor for component A in the absence of interactions. The latter is usually modeled as the static structure factor of a single Gaussian chain, i.e., $S_{eq}^{A}(q) = N_A f_D^A\,(q)$, where $f_D(q)$ is the Debye function. The situation is somewhat less straight forward in the spinodal region because the initial state, about which the linearization is implemented, is an unstable equilibrium state and $R(q) < 0$. $C_2(q)$ can still be expressed in terms of a negative virtual structure factor $S_x(q)$ using $C_2(q) = 2R(q)S_x(q)$, without any ambiguity. This is just replacing one unknown by another. Okada and Han[8] identified $S_x(q)$ as $S_{eq}(q)$ in Equation (17), which also changes sign in the spinodal region. The theoretical basis of this identification is somewhat unclear. We have shown that it corresponds to assuming that $C_2(q)$ remains constant during a temperature jump into the spinodal region, so that $C_2(q) = 2R_{in}(q)S_{eq}^{in}(q)$, where $R_{in}(q)$ and $S_{eq}^{in}(q)$ denote, respectively, the decay constant and the static structure factor in the initial equilibrium state, and can be calculated as explained above. For small temperature jumps, this approximation should be valid.

CONCLUDING REMARKS

The system size expansion which we used to obtain the proper Langevin equation for the description of fluctuations in nonlinear systems is valid as long as the magnitude of fluctuations is of order $\varepsilon^{1/2}$ as compared to the mean. Suziki[10] showed that before the inhomogeneous final equilibrium state is reached, there is a time interval (scaling regime) in which the magnitude of the fluctuations becomes comparable to the mean (fluctuation enhancement). The evolution of scaling functions was studied by Suziki.[10] The results presented in this paper are therefore applicable to the initial regime where ε-expansion is valid.

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A non-Markovian microscopic derivation of the linear Cahn-Hilliard-Cook theory is also possible with the projection operator formalisms. The final result for $\mathbf{S}(q,t)$ is similar to that in Equation (15):

$$\mathbf{S}(q,t) = \mathbf{S}_{\mathrm{eq}}(q) + \mathbf{L}(q,t)[\mathbf{S}_{\mathrm{in}}(q) - \mathbf{S}_{\mathrm{eq}}(q)\,\mathbf{L}^{\dagger}(q,t) \tag{18}$$

where $\mathbf{S}_{\mathrm{in}}(q)$ and $\mathbf{S}_{\mathrm{eq}}(q)$ are again the initial and final static structure matrices, and $\mathbf{L}(q)$ is the dynamic structure matrix, i.e., the time-displaced correlation matrix in the final equilibrium state with the normalization $\mathbf{L}(q,0) = \mathbf{I}$, and satisfies:

$$\mathbf{L}(q,t) = i\boldsymbol{\Omega}\mathbf{L}(q,t) - \int_{o}^{t} ds\, \mathbf{M}(q,t-s)\mathbf{L}(q,s),$$

where the frequency matrix $\boldsymbol{\Omega}$ and the memory matrix M have their usual microscopic definitions for a given set of dynamical variables in terms of the Liouville and projection operators.[11] In the microscopic derivation, the choice of the dynamical variable is less restrictive than in the macroscopic derivation, but the justification of the approximations inherent in Equation (18) is not as straightforward as in the macroscopic theory. The details of the microscopic derivation will be presented in a future publication.[12] The important conclusion in both derivations is that the time-dependence of $\mathbf{S}(q,t)$ during transients can be expressed in terms of the dynamic structure factor in the final equilibrium state quite generally. The latter does not have to relax exponentially. For example, if $\mathbf{L}(q,t)$ in one-component description can be described by superposition of two exponentials with relaxation rates Γ_1 and Γ_2, then $\mathbf{S}(q,t)$, according to Equation (15) or (18), will contain three exponential terms with decay constants $2\Gamma_1$, $2\Gamma_2$, and $\Gamma_1 + \Gamma_2$.

A final remark is that the derivations presented in this paper do not involve any model for the free energy of the mixture, such as the Flory-Huggins lattice model, and does not require the incompressibility assumption.

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