

Remarks on the structure and validity of the Cahn–Hilliard–Cook theory in multicomponent polymer systems

A. Ziya Akcasu*

Max-Planck-Institut für Polymerforschung, Postfach 3148, D-55021, Mainz, Germany

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The accuracy of the linear Cahn–Hilliard–Cook (CHC) theory in matrix form (multicomponent description) is scrutinized by comparing its exact macroscopic derivation with its phenomenological derivation based on the linear Markov process assumption. The effect of the coupling of density modes to those which are not directly observed is examined. The influence of the initial state on the accuracy of the CHC theory is discussed. Interpretation of scattering experiments using a bimodal description of transients is presented in detail. As an application, the possible effect of coupling to viscoelastic modes on transients is analysed. © 1997 Elsevier Science Ltd.

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Introduction

Because of their remarkable physical properties, multicomponent polymer systems have been the subject of numerous experimental and theoretical studies in recent years¹. The early stages of transients following an initial perturbation in such systems is studied in terms of the Cahn–Hilliard²–Cook³ (CHC) theory in matrix form. The matrix form is also used in multimodal description of transients, in which the coupling between the density modes and others, such as the viscoelastic modes, is taken into account explicitly. The purpose of this short paper is to discuss the structure and validity of the matrix formulation of the CHC theory, and to comment on its application to the interpretation of scattering experiments.

The transients after a perturbation in a mixture is monitored by measuring the scattering intensity $I(q, t)$ of a selected spatial mode. The intensity is proportional to the variance of the number-density fluctuations $a(\mathbf{q}, t)$ of the scattering centres in the Fourier space, i.e. $I(q, t) = \langle |a(\mathbf{q}, t)|^2 \rangle$, where the symbol $\langle \dots \rangle$ denotes the average over the initial perturbed distribution. In an incompressible binary mixture, $a(\mathbf{q}, t)$ is proportional to the composition variable or the order parameter. In an equilibrium state, $I(q, t)$ is independent of time, and equal to the static structure factor $S^{\text{eq}}(q) = \langle |a(\mathbf{q})|^2 \rangle_{\text{eq}}$. The relaxation of $I(q, t)$ from an initial intensity $I^{\text{in}}(q)$ after a perturbation to $S^{\text{eq}}(q)$ in the final equilibrium state is commonly represented by the CHC expression

$$I(t) = S^{\text{eq}} + [I^{\text{in}} - S^{\text{eq}}] e^{-2\lambda t} \quad (1)$$

where $\lambda = \lambda(q)$ is the relaxation frequency of the mode characterized by the wave number q . The explicit form of $\lambda(q)$ is not needed in the present discussion. In equation (1), and below, we suppress the q -dependence because the CHC theory, being a linear description, involves only

one spatial mode. The CHC form is obtained from the linear Langevin equation^{4,5} for fluctuation in $a(\mathbf{q}, t)$, which assumes that these fluctuations can be treated as a linear Markov process. The same mathematical framework leading to equation (1) shows^{4,5} that $\lambda(q)$ also describes the relaxation of the normalized dynamic scattering function (or the time-displaced density–density correlation function) $L^{\text{eq}}(q, t)$ in the final equilibrium state

$$L^{\text{eq}}(t) = \frac{\langle a(\mathbf{q}, t)a(\mathbf{q}, 0)^* \rangle_{\text{eq}}}{S^{\text{eq}}(q)} \quad (2)$$

according to

$$L^{\text{eq}}(t) = e^{-\lambda t} \quad (3)$$

Thus, the CHC expression can also be written as

$$I(t) = S^{\text{eq}} + [I^{\text{in}} - S^{\text{eq}}] L^{\text{eq}}(t)^2 \quad (4)$$

The characteristic and appealing feature of the CHC expression in this form is that it expresses the transients in the intensity following a perturbation, as a linear interpolation between the initial and final intensities with a time-dependent weighting function $[L^{\text{eq}}(t)]^2$, which is a measurable equilibrium property.

Microscopic basis of the CHC theory

The extension of the CHC theory to multicomponent or to multimodal systems is implemented by introducing a state vector $\mathbf{a}(\mathbf{q}, t) = \text{column}[a_1(\mathbf{q}, t), a_2(\mathbf{q}, t), \dots, a_n(\mathbf{q}, t)]$ to represent the fluctuations in a set of dynamical variables $a_j(\mathbf{q}, t)$, $j = 1, \dots, n$, and defining the intensity matrix as $\mathbf{I}(q, t) = \langle \mathbf{a}(\mathbf{q}, t)\mathbf{a}(-\mathbf{q}, t)^T \rangle$. The $a_j(\mathbf{q}, t)$ may denote the number densities of the different species in a multicomponent mixture, or the other modes that may be coupled to them. In order to investigate the nature of approximations inherent in the CHC theory in matrix form, we provided a microscopic derivation⁵ of $\mathbf{I}(q, t)$, using the Zwanzig⁶–Mori⁷ projection operator formalism

$$\mathbf{I}(t) = \mathbf{S}^{\text{eq}} + \mathbf{L}^{\text{eq}}(t)[\mathbf{I}^{\text{in}} - \mathbf{S}^{\text{eq}}]\mathbf{L}^{\text{eq}}(t)^T + \mathbf{R}(t) \quad (5)$$

*Permanent address and address for correspondence: University of Michigan, Department of Nuclear Engineering and Radiological Sciences, Ann Arbor, Michigan 48109-2104, USA

where $\mathbf{S}^{\text{eq}} = \langle \mathbf{a}(\mathbf{q})\mathbf{a}(-\mathbf{q})^T \rangle_{\text{eq}}$ denotes the static structure matrix, and

$$\mathbf{L}^{\text{eq}}(t) = \langle \mathbf{a}(\mathbf{q}, t)\mathbf{a}(-\mathbf{q}, 0)^T \rangle_{\text{eq}} \mathbf{S}^{\text{eq}}(\mathbf{q})^{-1} \quad (6)$$

denotes the normalized dynamic scattering matrix, both in the final equilibrium state. The $\mathbf{L}^{\text{eq}}(t)$ satisfies the generalized Langevin equation⁵⁻⁷

$$\frac{d\mathbf{L}^{\text{eq}}(t)}{dt} = i\mathbf{\Omega}(\mathbf{q})\mathbf{L}^{\text{eq}}(t) - \int_0^t du \mathbf{\Phi}(\mathbf{q}, t-u)\mathbf{L}^{\text{eq}}(u) \quad (7)$$

with the initial condition $\mathbf{L}^{\text{eq}}(0) = \mathbf{I}$ where \mathbf{I} is the identity matrix. In equation (7), $\mathbf{\Omega}(\mathbf{q})$ and $\mathbf{\Phi}(\mathbf{q}, t)$ are the usual frequency and memory matrices, respectively, in the projection operator formalism. Their microscopic equations are available⁵ but not needed for our discussions. The $\mathbf{R}(t)$ in equation (5) represents the remainder of an expansion obtained by an iteration procedure explained in ref. 5.

The important consequences of the microscopic derivation, which is exact, can be summarized as follows: (a) The first two terms in the expansion in equation (5) have the same structure as the conventional CHC expression in equation (4) in matrix form, representing an interpolation between the initial intensity matrix \mathbf{I}^{in} and the final equilibrium intensity matrix \mathbf{S}^{eq} through the time-dependent weighting function $\mathbf{L}^{\text{eq}}(t)$. We therefore regard these two terms as the *extension* of the CHC theory to multicomponent mixtures. (b) The matrix $\mathbf{R}(t)$ in equation (5) represents the correction to the CHC expression, and accounts for the effect of nonlinearities on the time evolution of $\mathbf{I}(t)$. The contribution to the latter of the other dynamical variables that are not in the set $\mathbf{a}(t)$ are also included in $\mathbf{R}(t)$. Since the expansion in equation (5) is not a perturbation series involving a smallness parameter⁵, the neglect of $\mathbf{R}(t)$ to obtain the CHC expression cannot be regarded as linearization, because $\mathbf{R}(t)$ contains terms of the same order as those appearing in the CHC expression. Other arguments of statistical nature are needed to justify the neglect of $\mathbf{R}(t)$ (CHC-approximation). We intend to clarify these statements in this communication later in terms of a phenomenological description. (c) The time evolution of the normalized dynamic scattering matrix $\mathbf{L}^{\text{eq}}(t)$, is non-Markovian in nature because of the memory effects represented by the memory matrix in equation (7). To clarify this point, we consider the one-component description, in which equation (5) reduces to

$$I(t) = S^{\text{eq}} + [I^{\text{in}} - S^{\text{eq}}]L^{\text{eq}}(t)^2 + R(t) \quad (8)$$

where $L^{\text{eq}}(t)$ satisfies the one dimensional form of equation (7). Contrary to the original CHC expression in equation (4), $L^{\text{eq}}(t)$ is not an exponential function of time in general. This non-Markovian behaviour of $L^{\text{eq}}(t)$ is a consequence of the memory term in equation (7). The memory effects for a given set of dynamical variables appear both in the time evolution of $L^{\text{eq}}(t)$ and in the remainder $R(t)$. (d) In order to quantitatively assess the validity of neglecting the remainder $\mathbf{R}(t)$ in equation (5) in obtaining the CHC form, one has to resort to a nonlinear microscopic description that takes into account the nonlinearities explicitly, such as the one introduced by Kawasaki⁸ some time ago by augmenting the set of variables $\{a_j\}$ by adding their products $a_j a_k, a_j a_k a_n, \dots$, to the state vector. In the microscopic description, which is based on the generalized Langevin

equation for the set $\{a_j\}$, the effect of nonlinearities are hidden in the random force. A detailed description of the nonlinear theory is beyond the purpose of this communication. Here, we only wish to compare the microscopic description to the more familiar phenomenological *linear* theory based on the *Markov* assumption, in order to elucidate the nature of approximations inherent in the CHC theory by obtaining an expression of the correction term $R(t)$ in equation (8).

Linear Markov description

When the fluctuations in a set of variables $\mathbf{a}(t)$ can be approximately described as linear vector Markov processes, the variance matrix of $\mathbf{a}(t)$ satisfies^{5,9,10}

$$\mathbf{I}(t) = \mathbf{S}^{\text{eq}} + \mathbf{L}^{\text{eq}}(t)[\mathbf{I}^{\text{in}} - \mathbf{S}^{\text{eq}}]\mathbf{L}^{\text{eq}}(t)^T \quad (9)$$

where $\mathbf{L}^{\text{eq}}(t)$ is given by

$$\mathbf{L}^{\text{eq}}(t) = e^{-\mathbf{\Lambda}t} \quad (10a)$$

and denotes as before the dynamic scattering matrix in the final equilibrium state⁵. The relaxation matrix $\mathbf{\Lambda}(\mathbf{q})$ can be obtained either from the Markov limit of equation (7) within the framework of the microscopic theory as

$$\mathbf{\Lambda}(\mathbf{q}) = i\mathbf{\Omega}(\mathbf{q}) - \int_0^\infty dt \mathbf{\Phi}(\mathbf{q}, t) \quad (10b)$$

or directly from the phenomenological linear Langevin equation for $\mathbf{a}(\mathbf{q}, t)$ in terms of the chemical potential and the q -dependent Onsager coefficient⁴. The expression of $\mathbf{\Lambda}(\mathbf{q})$ in equation (10b) can be considered as the microscopic definition of the q -dependent Onsager coefficients. A comparison of equations (5) and (9) shows that (a) the remainder $\mathbf{R}(t)$ is *zero* in the *linear Markov* process approximation, (b) $\mathbf{L}^{\text{eq}}(t)$ in equation (9) is expressible in terms of exponential functions with relaxation frequencies that are the eigenvalues of the relaxation matrix $\mathbf{\Lambda}(\mathbf{q})$, and (c) the correction term $\mathbf{R}(t)$ in equation (5) accounts for the effect of nonlinearities, as well as the memory effects arising from the non-Markovian evolution of the variables $\mathbf{a}(t)$. These effects are not included in the linear Markov description.

In order to further elucidate the origin of the correction term in equation (5), we again consider its one-component version given in equation (8). We then calculate, *using vector Markov description* in equation (9), the scattering intensity $I(t) = \langle |a_1(\mathbf{q}, t)|^2 \rangle$ of the *first component* $a_1(t)$, assuming that it is the only *visible* component among the dynamical variables $\mathbf{a}(t)$. By considering the first diagonal elements of both sides in equation (9), we obtain an alternative equation for $I(t)$

$$I(t) = S^{\text{eq}} + [I^{\text{in}} - S^{\text{eq}}]S^{\text{eq}}(t)^2 + R(t) \quad (11)$$

where $I^{\text{in}} = [I^{\text{in}}]_{11}$, $S^{\text{eq}} = [S^{\text{eq}}]_{11}$, and $S^{\text{eq}}(t)$ denotes the normalized dynamic scattering function of the visible component in the final equilibrium state

$$S^{\text{eq}}(t) = \frac{\langle a_1(\mathbf{q}, t)a_1(\mathbf{q}, 0)^* \rangle_{\text{eq}}}{\langle |a_1(\mathbf{q})|^2 \rangle_{\text{eq}}} \quad (12)$$

It is to be noted that $S^{\text{eq}}(t)$ is *not* equal to

$$L_{11}^{\text{eq}}(t) = [e^{-\mathbf{\Lambda}t}]_{11} \quad (13a)$$

in general. The relation between $S^{\text{eq}}(t)$ and $L_{11}^{\text{eq}}(t)$ is obtained from the definition of $\mathbf{L}^{\text{eq}}(t)$, i.e.

$$\mathbf{S}^{\text{eq}}(t) = \mathbf{L}^{\text{eq}}(t)\mathbf{S}^{\text{eq}} \quad (13b)$$

where $\mathbf{S}^{\text{eq}}(t) = \langle \mathbf{a}(\mathbf{q}, t) \mathbf{a}(-\mathbf{q}, 0)^T \rangle_{\text{eq}}$ is the unnormalized dynamic scattering matrix [see equation (6)]. Calculating the 1-1 element of both sides of equation (13b), we find

$$S^{\text{eq}}(t) = L_{11}^{\text{eq}}(t) + \sum_{j=2}^n L_{1j}^{\text{eq}}(t) \frac{S_{j1}^{\text{eq}}}{S_{11}^{\text{eq}}} \quad (14)$$

We observe that $S^{\text{eq}}(t) = L_{11}^{\text{eq}}(t)$ holds only when the visible component $a_1(t)$ is not *statically* coupled to the unobserved variables $a_j(t)$ for $j = 2, \dots, n$, i.e. when

$$S_{1j}^{\text{eq}} = 0, \quad \text{for } j > 1 \quad (15)$$

When this is not the case, the difference between $S^{\text{eq}}(t)^2$ and $L_{11}^{\text{eq}}(t)^2$ has to be included in the correction term $R(t)$ in equation (11). For simplicity, we present $R(t)$ only when equation (15) holds

$$R(t) = 2 \sum_{j=2}^n L_{1j}^{\text{eq}}(t) I_{j1}^{\text{in}} L_{11}^{\text{eq}}(t) + \sum_{j,k=2}^n L_{1j}^{\text{eq}}(t) [I_{jk}^{\text{in}} - S_{jk}^{\text{eq}}] L_{1k}^{\text{eq}}(t) \quad (16)$$

This equation shows explicitly the terms left out in the CHC theory by neglecting $R(t)$ in equation (11). However, the effect of nonlinearities is not included in equation (16), because $R(t)$ is obtained starting from the *linear* Markov description of the full set of variables. We first observe in equation (16) that the correction term involves possible initial coupling between the visible and unobserved components I_{j1}^{in} , $j \neq 1$, as well as the initial coupling among the unobserved components I_{jk}^{in} , $j, k \neq 1$. Depending on the way the *initial perturbed state* is produced in an experiment, I_{j1}^{in} may be zero, i.e. the visible component is not *statically* coupled to the unobserved variables in the initial state, as well as in the final equilibrium state. Even under this favourable condition, $R(t)$ reduces to

$$R(t) = \sum_{j,k=2}^n L_{1j}^{\text{eq}}(t) [I_{jk}^{\text{in}} - S_{jk}^{\text{eq}}] L_{1k}^{\text{eq}}(t) \quad (17)$$

This residual correction involves the static coupling I_{jk}^{in} and S_{jk}^{eq} , $j, k \neq 1$, among the unobserved variables. Even when the latter variables happen to be *orthogonal* to each other both in the initial and final states, i.e. when $I_{jk}^{\text{in}} = 0$ and $S_{jk}^{\text{eq}} = 0$ when $j \neq k$, there still remains

$$R(t) = \sum_{j=2}^n L_{1j}^{\text{eq}}(t)^2 [I_{jj}^{\text{in}} - S_{jj}^{\text{eq}}] \quad (18)$$

Since $L_{1j}^{\text{eq}}(t)$ and $S^{\text{eq}}(t)$ can be of the same order of magnitude in equation (11), $R(t)$ cannot be argued to be small as compared to the CHC terms. This observation confirms the general conclusion reached in the microscopic derivation that the CHC expression cannot be justified on the basis of linearization argument. However, the CHC approximation would be justified, at least asymptotically, if one could argue that the partial dynamic scattering functions $L_{1j}^{\text{eq}}(t)$ for $j \neq 1$ in equation (18) decay faster in time than $S^{\text{eq}}(t)$. The $L_{1j}^{\text{eq}}(t)$ for $t > 0$ denote the *dynamic coupling* between the observed and unobserved modes, because $L_{1j}^{\text{eq}}(0) = 0$ by virtue of the fact that $\mathbf{L}^{\text{eq}}(0)$ is diagonal. Hence, the correction term $R(t)$ vanishes at all times when the visible component is not *dynamically* coupled to the

unobserved variables. This happens when the non-diagonal elements λ_{1j} of the relaxation matrix $\mathbf{\Lambda}$ are zero. Indeed, by differentiating $L_{1j}^{\text{eq}}(t) = [e^{-\mathbf{\Lambda}t}]_{1j}$, we find $\dot{L}_{1j}^{\text{eq}}(t) = -\lambda_{1j} L_{1j}^{\text{eq}}(t)$ when $\lambda_{1j} = 0$ for $j > 1$. Since $L_{1j}^{\text{eq}}(0) = 0$, $L_{1j}^{\text{eq}}(t) = 0$ at all times for $j > 1$. The conclusion that $R(t) = 0$ when $L_{1j}^{\text{eq}}(t) = 0$ is true more generally, as can be seen from equation (16).

We now return to equation (11), and focus our attention on $S^{\text{eq}}(t) = [e^{-\mathbf{\Lambda}t}]_{11}$, which is the normalized dynamic scattering function in equilibrium of the visible component when the visible component is *statically* uncoupled from the unobserved variables. By expanding $e^{-\mathbf{\Lambda}t}$ into idempotents (i.e. spectral decomposition) one can express $S^{\text{eq}}(t)$ as a weighted average of exponential function¹¹. Thus, $S^{\text{eq}}(t)$ is non-exponential in general, as predicted in the microscopic theory (this result was differently interpreted in ref. 12). The non-exponential behaviour of $S^{\text{eq}}(t)$ is again due to the *dynamic* coupling between the visible and unobserved components. Indeed, in the absence of this coupling, i.e. when $\lambda_{1j} = 0$ for $j > 1$, $S^{\text{eq}}(t)$ is exponential: $S^{\text{eq}}(t) = \exp(-\lambda_{11}t)$.

It follows from these discussions that, when the visible component is dynamically and statically uncoupled from the unobserved variables, the correction term $R(t)$ vanishes at all times, and $S^{\text{eq}}(t)$ becomes exponential. This is expected because, in this case, the visible component $a_1(t)$ alone is a linear Markov process, and hence $I(t)$ is given by the one-dimensional CHC expression.

Bimodal description

In this section we discuss the implications of the above conclusions in the interpretation of scattering experiments, in which the final state is an equilibrium state, e.g. a step temperature change in one phase region. We assume that the fluctuations in the density of the labelled component, described by $a(t)$, are coupled to a slow mode, which we denote by $b(t)$ ¹³. In an incompressible binary mixture of two species, $a(t)$ is proportional to composition fluctuations, and the second component may represent the viscoelastic mode in the mixture. The intensity $I_{aa}(t) = \langle |a(t)|^2 \rangle$ is measured as a function of time for various values of q . The question we wish to answer is: how can we interpret these data, and what can we learn about the system from this interpretation?

The interpretation starts with equation (9) with the assumption that the fluctuations in the variable $a(t)$ and $b(t)$ can be jointly treated as a linear Markov process. We reproduce equation (9) in a more compact form

$$\Delta(t) = \mathbf{L}^{\text{eq}}(t) \Delta(0) \mathbf{L}^{\text{eq}}(t)^T \quad (19a)$$

where

$$\Delta(t) = \mathbf{I}(t) - \mathbf{S}^{\text{eq}} \quad (19b)$$

and $\Delta(0) = \mathbf{I}^{\text{in}} - \mathbf{S}^{\text{eq}}$. The normalized scattering matrix $\mathbf{L}^{\text{eq}}(t)$, which is defined in equation (10a), can be written as a linear superposition of two exponentials. The coefficients can be easily obtained using $\mathbf{L}^{\text{eq}}(0) = \mathbf{I}$ and $\dot{\mathbf{L}}^{\text{eq}}(0) = -\mathbf{\Lambda}$

$$\mathbf{L}^{\text{eq}}(t) = \frac{1}{\lambda_1 - \lambda_2} [(\mathbf{\Lambda} - \lambda_2 \mathbf{I}) e^{-\lambda_1 t} - (\mathbf{\Lambda} - \lambda_1 \mathbf{I}) e^{-\lambda_2 t}] \quad (20)$$

The relaxation frequencies λ_1 and λ_2 are the eigenvalues

of the 2×2 relaxation matrix Λ , i.e. the roots of $\lambda^2 - (\Lambda_{aa} + \Lambda_{bb})\lambda + |\Lambda| = 0$, where $|\Lambda| = \Lambda_{aa}\Lambda_{bb} - \Lambda_{ab}\Lambda_{ba}$. In general, Λ is not symmetric.

The measured intensity $I_{aa}(t) = S_{aa}^{eq} + \Delta_{aa}(t)$ is obtained from equation (19a) as

$$I_{aa}(t) = S_{aa}^{eq} + \Delta_{aa}(0)L_{aa}^{eq}(t)^2 + 2\Delta_{ab}(0)L_{aa}^{eq}(t)L_{ab}^{eq}(t) + \Delta_{bb}(0)L_{ab}^{eq}(t)^2 \quad (21)$$

where all the quantities on the left are defined in terms of the elements $\Lambda_{aa}, \Lambda_{ab}, \Lambda_{ba}, \Lambda_{bb}$, the initial intensities $I_{aa}^{in}, I_{ab}^{in} = I_{ba}^{in}, I_{bb}^{in}$, and the partial structure factors $S_{aa}^{eq}, S_{ab}^{eq} = S_{ba}^{eq}, S_{bb}^{eq}$ in the final equilibrium state. Thus, if $I_{aa}^{in}, I_{ab}^{in}, I_{bb}^{in}$ were known from the initial preparation of the system, and $S_{aa}^{eq}, S_{ab}^{eq}, S_{bb}^{eq}$ were independently calculated in the final equilibrium state, using, for example, the random phase approximation, then the matrix elements $\Lambda_{aa}, \Lambda_{ab}, \Lambda_{ba}, \Lambda_{bb}$ would be the unknown dynamic quantities to be extracted from the data. Since $L^{eq}(t)$ is expressed in equation (20) as the superposition of two exponentials, $I_{aa}(t)$ contains three exponentials

$$I_{aa}(t) = S_{aa}^{eq} + A_1 e^{-2\lambda_1 t} + A_2 e^{-(\lambda_1 + \lambda_2)t} + A_3 e^{-2\lambda_2 t} \quad (22)$$

where the expressions of the prefactors A_1, A_2 and A_3 are too lengthy to be written down explicitly. Their calculation, however, is straightforward. From $I_{aa}(0)$, we have the following relation among them

$$A_1 + A_2 + A_3 = I_{aa}^{in} - S_{aa}^{eq} \quad (23a)$$

If that initial slope $\dot{I}_{aa}(0)$ of $I_{aa}(t)$, can also be extracted from the data with sufficient accuracy, we have another relation

$$\dot{I}_{aa}(0) = -2\lambda_1 A_1 - (\lambda_1 + \lambda_2)A_2 - 2\lambda_2 A_3 \quad (23b)$$

Equations (21), (22) and (23) are all what the bimodal description offers for the interpretation of the data. By an appropriate curve-fitting procedure with the constraints given in equations (23), one can determine A_1, A_2, A_3 and λ_1, λ_2 from the data, which can then be used to check a given physical model regarding the nature of the second mode. This procedure may be too ambitious, and lacks numerical accuracy required for the determination of the parameters. The following simpler models may be justified depending on the initial conditions:

(a) Both $\Delta_{ab}(0) = \Delta_{ba}(0)$ and $\Delta_{bb}(0)$ vanish. This case corresponds to a situation in which the initial perturbation does not influence the second mode so that $I_{ab}(0) = I_{ab}^{in} \cong S_{ab}^{eq}$ and $I_{bb}(0) = I_{bb}^{in} \cong S_{bb}^{eq}$. It may be realized when the system is prepared initially in an equilibrium state at an initial temperature T_i , so that $I_{ab}^{in} = S_{ab}^{eq}(T_i)$ and $I_{bb}^{in} = S_{bb}^{eq}(T_i)$ (step temperature changes within the homogeneous phase), and $S_{ab}^{eq}(T_i) \cong S_{ab}^{eq}(T_f)$ and $S_{bb}^{eq}(T_i) \cong S_{bb}^{eq}(T_f)$. If the second mode represents the effect of the internal modes, these conditions may more likely be satisfied. Then, equation (21) reduces to

$$L_{aa}^{eq}(t) = \left[\frac{I_{aa}(t) - S_{aa}^{eq}}{I_{aa}(0) - S_{aa}^{eq}} \right]^{1/2} \quad (24)$$

where

$$L_{aa}^{eq}(t) = \frac{1}{\lambda_1 - \lambda_2} [(\Lambda_{aa} - \lambda_2) e^{-\lambda_1 t} - (\Lambda_{aa} - \lambda_1) e^{-\lambda_2 t}] \quad (25)$$

We recall that $L_{aa}^{eq}(t) \neq S_{aa}^{eq}(t)/S_{aa}^{eq}$, unless the two

components are *uncoupled* (or orthogonal) in the final equilibrium state, i.e. $S_{ab}^{eq} = 0$, as discussed above [see equations (14) and (15)]. When this is the case, $L_{aa}^{eq}(t)$ becomes the normalized dynamic structure factor of the visible component in the final equilibrium, for which analytical expressions are often available by independent calculations. For example, the case, in which the second component represents the effect of the internal modes of chains, was discussed in detail in ref. 5. Muller *et al.*¹⁴ showed recently that the observed deviation of $L_{aa}^{eq}(t)$ from a single exponential is not due to the coupling of concentration fluctuations to the internal modes in the q -range considered in their experiments.

As an alternative model, we propose that one in which the visible component is coupled to the viscoelastic modes¹⁵. In this model, the normalized dynamic scattering function is represented by¹⁶

$$L_{aa}^{eq}(t) = \frac{1}{\lambda_1 - \lambda_2} [(\Omega(q) - \lambda_2) e^{-\lambda_1 t} - (\Omega(q) - \lambda_1) e^{-\lambda_2 t}] \quad (26)$$

where $\Omega(q) = q^2 D_c$ denotes the first cumulant; $\lambda_1 \lambda_2 = q^2 D_c / T_r$; $\lambda_1 + \lambda_2 = q^2 D_g + T_r^{-1}$. In these definitions, $D_c = E_{0s} / f$ denotes the collective diffusion coefficient, whereas E_{0s} and f are the osmotic modulus and friction coefficient; $D_g = (E_{0s} + E_g) / f$ denote the pseudo gel diffusion coefficient^{17,18}, where E_g is the longitudinal bulk modulus; T_r is taken to be the characteristic lifetime of the entanglements in the transient network^{17,18}.

In this model the viscoelastic mode is approximated by $\eta(t) = E_g \exp(-t/T_r)$. In the absence of the coupling, i.e. when $E_g = 0$, $\lambda_1 = q^2 D_c$ and, although irrelevant in this case, $\lambda_2 = T_r^{-1}$. We note that in general λ_1 and λ_2 cannot be identified as the collective diffusion coefficient and the viscoelastic relaxation frequency, because of the coupling between these two modes.

The analytical results presented in this article are also applicable to the early stages of spinodal decomposition, provided the final equilibrium state S^{eq} is interpreted as the *virtual* equilibrium state^{5,19}. The latter is the analytic continuation of S^{eq} obtained by evaluating S^{eq} at the final temperature¹⁹. In the case of bimodal description with coupling to viscoelastic mode, the collective diffusion coefficient $D_c(q)$ becomes negative when $q < q_c$ in the spinodal region. This implies that $L_{aa}^{eq}(t)$ consists of one growing exponential ($\lambda_1 < 0$), and one decaying one because $\lambda_2 > 0$ always holds even when $\lambda_1 < 0$. In conclusion, equations (24) and (26) may be used to interpret experimental data when coupling to viscoelastic modes is expected to be important in a polymer mixture.

(b) $\Delta_{ab}(0) = \Delta_{ba}(0) = 0$. This is a less restrictive case in which the two components are statically uncoupled both in the initial and final equilibrium state, i.e. $S_{ab}^{eq} = 0$ and $I_{ab}^{in} = 0$, and hence $\Delta_{ab}(0) = 0$. But $\Delta_{bb}(0) = I_{bb}^{in} - S_{bb}^{eq} = 0$ is not assumed, so that the initial perturbation is allowed to affect the unobserved variable. In this case, the measured intensity follows from equation (21) as

$$I_{aa}(t) = S_{aa}^{eq} + \Delta_{aa}(0)L_{aa}^{eq}(t)^2 + \Delta_{bb}(0)L_{ab}^{eq}(t)^2 \quad (27)$$

The last term arises from the *dynamic* coupling between the two modes, as discussed above. It represents the relaxation of the initial perturbation $\Delta_{bb}(0) = S_{bb}^{eq}(T_i) - S_{bb}^{eq}(T_f)$ which is due to the change in the static structure

factor of the second component from the initial to final temperature during the step change. The expression of $L_{ab}^{eq}(t)$ for $t > 0$ follows from equation (20) as

$$L_{ab}^{eq}(t) = \frac{\Lambda_{ab}}{\lambda_1 - \lambda_2} [e^{-\lambda_1 t} - e^{-\lambda_2 t}] \quad (28)$$

As stated previously, the dynamic coupling between the modes is accounted for by Λ_{ab} . Indeed, when the latter vanishes, $L_{ab}^{eq}(t) = 0$ at all times. The first term in equation (27) represents the decay of the initial perturbation $\Delta_{aa}(0) = S_{aa}^{eq}(T_i) - S_{aa}^{eq}(T_f)$ in the visible component. In the absence of the dynamic coupling, equation (27) reduces to equation (24), with

$$L_{aa}^{eq}(t) = e^{-\Lambda_{aa} t}$$

instead of equation (25). This is because the eigenvalues of Λ are $\lambda_1 = \Lambda_{aa}$ and $\lambda_2 = \Lambda_{bb}$ when it is diagonal, and the last term in equation (25) vanishes, i.e. the visible component is itself a Markov process.

Conclusions

In this paper, we have discussed the structure and the validity of the CHC expression in matrix form. We have shown that CHC expression becomes exact in matrix form when the time evolution of the state vector can jointly be treated as a linear vector Markov process. Otherwise, it is approximate, and the correction term is due to nonlinearities, as well as to the memory effects representing the influence of the unobserved variables on the time evolution of the observed variables. It is concluded that the validity of the CHC theory is improved by including all the unobserved slowly varying variables that are coupled to the visible components, so that the augmented set can be treated as a linear vector Markov process. We have shown that the validity of the CHC expression for a given set of variables strongly depends on the preparation of the initial state, and the degree

of static and dynamic coupling between observed and unobserved variables. We have presented the bimodal description in general, and analysed, as a possible model for polymer mixtures with entanglement, the special case in which the density is coupled to the viscoelastic mode in detail.

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References

1. Takenaka, M. and Chu, B., *Macromolecules*, 1995, **28**, 3240.
2. Cahn, J. W. and Hilliard, J. E., *J. Chem. Phys.*, 1958, **28**, 258; 1959, **31**, 688; Cahn, J. W., *J. Chem. Phys.*, 1965, **42**, 93.
3. Cook, H. E., *Acta Metall.*, 1970, **18**, 297.
4. Binder, K., *J. Chem. Phys.*, 1983, **79**, 6387.
5. Akcasu, A. Z., *Macromolecules*, 1989, **22**, 3682.
6. Zwanzig, R., *Lectures in Theoretical Physics*, ed. W. E. Britten, W. D. Downs and J. Downs, Vol. 3. Wiley, New York, 1961, p. 106.
7. Mori, M., *Prog. Theoret. Phys. (Kyoto)*, 1965, **33**, 423.
8. Kawasaki, K., *Ann. Phys. (New York)*, 1970, **61**, 1.
9. Akcasu, A. Z., *J. Stat. Phys.*, 1977, **16**, 33.
10. Lax, M., *Rev. Mod. Phys.*, 1960, **32**, 25.
11. Akcasu, A. Z., Nägele, G. and Klein, R., *Macromolecules*, 1991, **24**, 4408.
12. Jäckle, J. and Pieroth, M. Z., *Phys. B-Condensed Matter*, 1988, **72**, 25.
13. Binder, K., Frisch, H. L. and Jäckle, J., *J. Chem. Phys.*, 1986, **85**, 3.
14. Müller, G., Schwahn, D., Eckerlebe, H., Rieger, J. and Springer, T., *J. Chem. Phys.*, 1996, **104**, 5326. See also: Schwahn, D., Janssen, S. and Springer, T., *J. Chem. Phys.*, 1992, **97**, 8775.
15. Brown, W. and Nicoli, T., in *Dynamic Light Scattering*, Ch. 6, ed. W. Brown. Oxford University Press, Oxford, 1993.
16. Akcasu, A. Z., Klein, R. and Wang, C. H., *Macromolecules*, 1994, **27**, 2736.
17. Brochard, F. and de Gennes, P.-G., *Macromolecules*, 1977, **10**, 1157.
18. Adam, M. and Delsanti, M., *Macromolecules*, 1985, **18**, 1760.
19. Okada, M. and Han, C. C., *J. Chem. Phys.*, 1986, **85**, 5317.