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Remarks on the "Fast" and "Slow" Mode Theories of Interdiffusion

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1. Introduction

The interdiffusion process accounts for the relaxation of thermal fluctuations in the composition of a binary fluid. It describes the mixing of the components in the mixture through an interdiffusion coefficient $D_{\mathrm{int}} = Q\Lambda$ where Q is a thermodynamic factor related to the static correlation function of composition fluctuations, and Λ is a kinetic factor presumed to be expressible in terms of the molecular (i.e., polymer) tracer-diffusion coefficients D_A and D_B of the components in the mixture. However, there is no general basis to expect such a relation to exist except for some limiting cases.[1−3] This statement holds in Liouville dynamics as well as in Smoluchowski dynamics. Early attempts to express Λ in terms of D_A and D_B result in two different contradictory analytical forms which have been referred to in the literature[4] as the "slow" and "fast" mode theories. The slow mode result is obtained with the random-phase approximation (RPA) under the condition of microscopic incompressibility as

$$1/\Lambda_{\mathrm{slow}} = \Phi_B/(D_A N_A) + \Phi_A/(D_B N_B) \tag{1}$$

where Φ_A and Φ_B are the volume fractions, defined as $\Phi_\alpha = n_\alpha/(n_A + n_B)$, where n_α is the total number of monomers in the αth component, and N_A and N_B are the polymerization indices of the constituent polymers of the blend. The fast mode result is obtained by ignoring the dynamic correlations between the velocities of different particles as

$$\Lambda_{\mathrm{fast}} = \Phi_B D_A N_A + \Phi_A D_B N_B \tag{2}$$

A comparison of eqs 1 and 2 shows that when $D_A \ll D_B$, $\Lambda_{\mathrm{slow}} \to D_A N_A/\Phi_B$, i.e., dominated by the slow mode D_A, whereas $\Lambda_{\mathrm{fast}} \to \phi_A D_B N_B$, i.e., dominated by the fast mode. Two different expressions for the interdiffusion coefficient in binary fluids have recently been proposed by Akcasu, Nägele, and Klein[2] (ANK) and by Brereton[5] (B), both of which recapture the results of the fast and slow mode theories as the two limiting cases. The ANK expression is obtained by applying the RPA to an incompressible ternary mixture, with the third component treated as vacancies. In the case of unentangled chains, it reads

$$\Lambda = \Phi_A \Phi_B \left[\frac{D_A N_A}{\Phi_A} + \frac{D_B N_B}{\Phi_B} - \frac{(D_A N_A - D_B N_B)^2}{\Phi_A D_A N_A + \Phi_B D_B N_B + \Phi_C D_C N_C} \right] \tag{3}$$

where $\Phi_C = n_C/(n_A + n_B)$, D_C and N_C denote the volume fraction relative to that of A and B monomers together, the molecular tracer-diffusion coefficient in the mixture, and the degree of polymerization of the third component. We note that Φ_C varies from 0 to infinity, when the total number of C monomers, n_C, is increased. Although the meaning of D_C and N_C becomes obscure when the third component is treated as vacancies, the ANK expression recovers the slow and fast mode results in the limit of $\Phi_C \to 0$ and $\Phi_C \to \infty$, respectively, regardless of the interpretation of D_C and N_C. Since the vacancy concentration increases with the experimental temperature T above the glass transition temperature T_g, the ANK expression predicts the fast mode result far above T_g, with a gradual transition to the slow mode results as $T \to T_g$. The overall molecular weight dependence of Λ in PS/PVME mixtures was found by Feng et al.[6] in their light scattering experiments to be well in accord with the ANK equation. More recently, another relation between Λ and the tracer-diffusion coefficients in pure melts of the components was found by Brereton[5] in the following form:

$$1/\Lambda = (1 - U)/\Lambda_{\mathrm{slow}} + U/\Lambda_{\mathrm{fast}} \tag{4}$$

where Λ_{slow} and Λ_{fast} are defined in eqs 1 and 2. In this equation the parameter $U(T)$ is a measure of the closeness of the glass transition T_g to the experimental temperature T. Far above the glass transition, $U(T) \to 0$ so that the slow mode result is predicted by the B expression. This prediction is in contradiction with the fast mode result predicted by the ANK expression under identical experimental conditions. Meier et al.[7] have reported recently that their experiments in the low molecular weight PDMS/PEMS blends far above T_g are consistent with the fast mode result and hence favor the ANK result. The controversy on the fast and slow mode theories would have been finally resolved by the more general expressions of the interdiffusion coefficient in eqs 3 and 4, both displaying a continuous transition from the fast to slow mode limit as a function of the vacancy concentration, had they not predicted contradictory trends. Although the existing experimental evidence seems to favor the ANK expression, it is still desirable to understand theoretically the origin of this discrepancy. It is the purpose of this work to scrutinize the foundations of the ANK and B theories in order to understand why they lead to contradictory results under identical experimental conditions, even though they are both based on mean-field type arguments.

2. Discussion

The B theory is based on the positional (or overdamped) Langevin equation for the position vectors $\mathbf{r}_j^\alpha$ of the monomers (particles) in each component α = A, B. For simplicity we consider for the moment a simple one-component system of N particles in a volume Ω in the following discussions:

$$\nu \frac{\mathrm{d}}{\mathrm{d}t} \mathbf{r}_j(t) = \mathbf{F}_j(\mathbf{r}^N(t)) + \xi_j(t) \tag{5}$$

where ν is the friction coefficient of a particle in the actual mixture, $\mathbf{F}_j(\mathbf{r}^N)$ is the force acting on the jth particle due to the interactions between the particle pairs, $\mathbf{r}^N = \{\mathbf{r}_1, ..., \mathbf{r}_N\}$, and $\xi_j(t)$ is the stochastic Langevin force (internal noise). In the case of a Brownian particle submerged in a fluid, $\xi_j(t)$ represents the fluctuating part of the force exerted on the Brownian particle by the solvent, the mean force being represented by the term $\nu\, \mathrm{d}\mathbf{r}_j/\mathrm{d}t$ (hydrodynamic interaction between

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particles being ignored). The meaning of eq 5 therefore becomes obscure when it is written for the monomers in melt, in which there is no solvent to provide the additional Langevin force. Indeed, the positional Langevin equations (5) as applied to suspensions of Brownian particles invoke a separation of time scales in that the particle velocity correlation functions are assumed to relax much faster toward equilibrium than the positional degrees of freedom. This implies that eq 5 is valid only for correlation times $t \gg \tau_B$, where τ_B denotes a characteristic momentum relaxation time. All the interparticle interactions are accounted for by $\mathbf{F}_j(\mathbf{r}^N)$. We therefore believe that eq 5 is not an appropriate starting point for the dynamics of melts.

Another objection arises from the use of the fluctuation–dissipation theorem in the B theory as written in eq 5 of ref 5:

$$\langle \xi_j(t)\, \xi_k^{\mathrm{T}}(0)\rangle = kT\nu_0\delta(t)\, \mathbf{1}\delta_{jk} \tag{6}$$

where ν_0 is introduced as a "bare friction coefficient", different from ν, and the superscript T denotes the operation of transposition. Moreover, **1** denotes the three-dimensional unit matrix. The fluctuation–dissipation theorem does not allow such a distinction and, in fact, requires ν_0 to be equal to 2ν. This requirement follows from the fact that the equilibrium configuration space distribution function, $\psi_{\mathrm{eq}}(\mathbf{r}^N) \sim \exp[-\beta U(\mathbf{r}^N)]$, must satisfy the Smoluchowski (or Kirkwood–Riseman) equation which is derived from eq 5 under the additional assumption that $\xi_j(t)$ is a Gaussian random process as

$$\frac{\partial\psi(\mathbf{r}^N,t)}{\partial t} = -\frac{1}{\nu}\frac{\partial}{\partial \mathbf{r}_j}\cdot[\mathbf{F}_j(\mathbf{r}^N)\,\psi(\mathbf{r}^N,t)] + \frac{1}{2}\frac{k_{\mathrm{B}}T\nu_0}{\nu^2}\frac{\partial}{\partial \mathbf{r}_j}\cdot\frac{\partial}{\partial \mathbf{r}_j}\,\psi(\mathbf{r}^N,t) \tag{7}$$

with $\mathbf{F}_j(\mathbf{r}^N) = -\partial U(\mathbf{r}^N)/\partial \mathbf{r}^j$ and where summation over repeated indices is understood. Since the relationship between the proposed mean-field glass transition and the friction coefficient, i.e., eq 20 of ref 5, is based on the distinction between ν_0 and ν, the requirement $\nu_0 = 2\nu$ completely invalidates eq 20 and the main conclusion of the B theory that the interdiffusion coefficient must be calculated according to the slow mode theory sufficiently above the glass transition temperature.

The concept of a mean-field glass transition, which is introduced through eq 17 of ref 5, in the B theory is indeed intriguing. It may therefore be informative to investigate the physical content of this equation more closely in light of the above discussion. Introducing the long-time self-diffusion coefficient $D_{\mathrm{S}}^{\mathrm{L}}$ through

$$D_{\mathrm{S}}^{\mathrm{L}} = \frac{1}{3}\int_0^\infty \mathrm{d}t\, \langle\langle \mathbf{v}_j(t)\cdot\mathbf{v}_j(0)\rangle\rangle \tag{8}$$

and using eq 5 to express $\mathbf{v}_j(t)$ in terms of forces, one obtains

$$D_{\mathrm{S}}^{\mathrm{L}} = D_{\mathrm{S}}^{\mathrm{S}} + \frac{1}{3\nu^2}\int_0^\infty \mathrm{d}t\, [\langle\langle \mathbf{F}_j(t)\cdot\mathbf{F}_j(0)\rangle\rangle + \langle\langle \mathbf{F}_j(t)\cdot\xi_j(0)\rangle\rangle + \langle\langle \xi_j(t)\cdot\mathbf{F}_j(0)\rangle\rangle] \tag{9}$$

where $D_{\mathrm{S}}^{\mathrm{S}} = k_{\mathrm{B}}T/\nu$ is the short-time self-diffusion coefficient. In eq 9 the symbol $\langle\langle\cdots\rangle\rangle$ implies averaging with respect to the realizations of $\xi_j(t)$, as well as an equilibrium averaging over the initial configuration $\{\mathbf{r}^N(0)\}$ of the particles.[8] The last term in the integrand vanishes because $\mathbf{r}^N(0)$ is not correlated with the future realizations of $\xi_j(t)$. For the sake of clarity we mention that $D_{\mathrm{S}}^{\mathrm{L}}$ is defined as the long-time limit of $\langle|\Delta\mathbf{r}_j(t)|^2\rangle/6t$, where $\langle|\Delta\mathbf{r}_j(t)|^2\rangle$ is the mean-square displacement. Note that the autocorrelation $\langle\langle \mathbf{F}_j(t)\cdot\mathbf{F}_j(0)\rangle\rangle$ is necessarily positive valued when calculated within the framework of the overdamped Langevin equation or the stochastically equivalent Smoluchowski equation.

Hence, the neglect of the cross-correlation $\langle\langle \mathbf{F}_j(t)\cdot\xi_j(0)\rangle\rangle$ would imply a long-time self-diffusion coefficient which is larger than the short-time self-diffusion coefficient. However, on physical grounds it is expected that $D_{\mathrm{S}}^{\mathrm{L}} < D_{\mathrm{S}}^{\mathrm{S}}$ since the self-diffusion of a Brownian particle is hindered for long times by its many collisions (i.e., potential interactions) with neighboring particles.

In fact, an exact calculation gives the result

$$D_{\mathrm{S}}^{\mathrm{L}} = D_{\mathrm{S}}^{\mathrm{S}} - \int_0^\infty \mathrm{d}t\, \langle \mathbf{F}_j\cdot \mathrm{e}^{O^\dagger(\mathbf{r}^N)t}\mathbf{F}_j\rangle_k < D_{\mathrm{S}}^{\mathrm{S}} \tag{10}$$

where $O^\dagger(\mathbf{r}^N)$ is the adjoint of the differential operator which appears on the right-hand side of the Smoluchowski equation (7), and $\langle\cdots\rangle_k$ denotes the canonical equilibrium average over the particle positions.

Explicitly, the adjoint operator is

$$O^\dagger(\mathbf{r}^N) = D^0\sum_{l=1}^{N}\left[\frac{\partial}{\partial \mathbf{r}_l} + \frac{1}{k_{\mathrm{B}}T}\mathbf{F}_l(\mathbf{r}^N)\right]\cdot\frac{\partial}{\partial \mathbf{r}_l} \tag{11}$$

where $D^0 = k_{\mathrm{B}}T/\nu_0$ is the Stokesian diffusion coefficient.

If one introduces a long-time friction coefficient ν_{L} through $D_{\mathrm{S}}^{\mathrm{L}} = k_{\mathrm{B}}T/\nu_{\mathrm{L}}$, then eq 9 can be written as

$$\frac{1}{\nu_{\mathrm{L}}} = \frac{1}{\nu} + \frac{1}{3k_{\mathrm{B}}T\nu^2}\int_0^\infty \mathrm{d}t\, [\langle\langle \mathbf{F}_j(t)\cdot\mathbf{F}_j(0)\rangle\rangle + \langle\langle \mathbf{F}_j(t)\cdot\xi_j(0)\rangle\rangle] \tag{12}$$

If one had distinguished between ν_0 and ν and had interpreted the long-time diffusion coefficient as $D_{\mathrm{S}}^{\mathrm{L}} = k_{\mathrm{B}}T/\nu$, then eq 12 would become

$$\nu = \nu_0 + \frac{1}{3k_{\mathrm{B}}T}\int_0^\infty \mathrm{d}t\, [\langle\langle \mathbf{F}_j(\mathbf{r}^N(t))\cdot\mathbf{F}_j(\mathbf{r}^N(0))\rangle\rangle + \langle\langle \mathbf{F}_j(\mathbf{r}^N(t))\cdot\xi_j(0)\rangle\rangle] \tag{13}$$

This is eq 17 of ref 5, except for the last term. One can easily demonstrate that $\langle\langle \mathbf{F}_j(t)\cdot\xi_j(0)\rangle\rangle$ does not vanish and that it cannot be neglected, by considering simple tractable examples, such as a Gaussian dumbbell consisting of two particles connected by a spring. In this example, the Langevin equations are

$$\nu\dot{\mathbf{r}}_1 = -k(\mathbf{r}_1 - \mathbf{r}_2) + \xi_1(t) \tag{14}$$

$$\nu\dot{\mathbf{r}}_2 = k(\mathbf{r}_1 - \mathbf{r}_2) + \xi_2(t) \tag{15}$$

with

$$\langle \xi_i(t)\, \xi_j(t')\rangle = 2\nu k_{\mathrm{B}}T\mathbf{1}\delta_{ij}\delta(t - t') \tag{16}$$

where k is the spring constant, and $\mathbf{F}_1 = -\mathbf{F}_2 = k(\mathbf{r}_1 - \mathbf{r}_2)$. Expressing these equations in terms of center of mass and relative position vectors, one can show that for $t > 0$

$$\langle\langle \mathbf{F}_j(t)\cdot\mathbf{F}_j(0)\rangle\rangle = 3kk_{\mathrm{B}}T\exp(-2kt/\nu) \tag{17}$$

$$\langle\langle \mathbf{F}_j(t)\cdot\xi_j(0)\rangle\rangle = -6kk_{\mathrm{B}}T\exp(-2kt/\nu) \tag{18}$$

Substituting eqs 17 and 18 into eq 12 yields $\nu_{\mathrm{L}} = 2\nu$, so that the long-time diffusion coefficient becomes $D_{\mathrm{S}}^{\mathrm{L}} = D_{\mathrm{S}}^{\mathrm{S}}/2$. The latter is, of course, the translational diffusion coefficient of a dumbbell in the absence of hydrodynamic interaction. The above example shows that the neglect of $\langle\langle \mathbf{F}_j(t)\cdot\boldsymbol{\xi}_j(0)\rangle\rangle$ in eq 12 or in the corresponding equation in the B theory cannot be categorically justified. Another nontrivial example which elucidates this point is given by a dilute suspension of hard spheres of radius a and volume fraction $\phi = (4\pi/3)\bar{\varrho}a^3$, where $\bar{\varrho}$ is the mean number density of spheres. The long-time self-diffusion coefficient is given to leading order in ϕ as

$$D_S^{L} = D^0(1 - 2\phi) \qquad (19)$$

where $D^0 = k_BT/6\pi\eta a$ denotes the free diffusion coefficient, and η is the shear viscosity of the solvent.[9] Clearly $D_S^L < D^0$. In deriving this result, hydrodynamic interaction has been ignored.

We also wish to comment on the calculation of the partial dynamic structure factors and of the interdiffusion coefficient in the B theory. The Langevin equation for the density fluctuations (for $\mathbf{q} \neq 0$)

$$\varrho_{\mathbf{q}} = \frac{1}{\Omega}\sum_{j=1}^{N} e^{i\mathbf{q}\cdot\mathbf{r}_j} \qquad (20)$$

is obtained from eq 5 as (eq 6 of ref 5)

$$\dot{\varrho}_{\mathbf{q}} = -\frac{1}{\nu}\sum_{\mathbf{k}}(\mathbf{k}\cdot\mathbf{q})V_{\mathbf{k}}\varrho_{\mathbf{k}+\mathbf{q}}\varrho_{-\mathbf{k}} + n_{\mathbf{q}}(t) \qquad (21)$$

where

$$V_{\mathbf{k}} = \int_{\Omega} d^3r\, e^{i\mathbf{k}\cdot\mathbf{r}}V(r) \qquad (22)$$

is the Fourier component of the pair-interaction potential $V(r)$, and

$$n_{\mathbf{q}}(t) = \frac{1}{\Omega}\sum_{j=1}^{N} i\mathbf{q}\cdot\boldsymbol{\xi}_j(t)\, e^{i\mathbf{q}\cdot\mathbf{r}_j(t)} \qquad (23)$$

Note that $\boldsymbol{\xi}_j(t)$ is now multiplied by a function of $\mathbf{r}_j(t)$, which itself depends on the previous history of $\boldsymbol{\xi}_j(t)$. Hence, $n_{\mathbf{q}}(t)$ is in contrast to $\boldsymbol{\xi}_j(t)$, a multiplicative noise, and therefore requires more care.

The term $n_{\mathbf{q}}(t)$ is referred to as the "heat bath terms" in ref 5, and its statistical properties are not explicitly discussed in the B theory. It appears that the following properties, usual for white noise thermal bath forces,

$$\langle n_{\mathbf{q}}(t)\rangle = 0 \qquad (24)$$

$$\langle n_{\mathbf{q}}(t)\, \varrho_{-\mathbf{q}}(0)\rangle = 0 \qquad (25)$$

in particular, are used in the calculation of dynamic correlation functions (eqs 10 of ref 5).

Since the statistical properties of $n_{\mathbf{q}}(t)$ are crucial in these calculations, we demonstrate again in a special limit that the properties in eqs 24 and 25 do not hold. We consider a collection of noninteracting particles, so that $\mathbf{F}_j = 0$, in the Langevin equations (5):

$$\nu\frac{d\mathbf{r}_j}{dt} = \boldsymbol{\xi}_j(t) \qquad (26)$$

Substituting the explicit solution for $\mathbf{r}_j(t)$ from this equation into the expression for $n_{\mathbf{q}}(t)$ yields for its average over the realizations of $\boldsymbol{\xi}_j(t)$

$$\langle n_{\mathbf{q}}(t)\rangle = \frac{1}{\Omega}\sum_{j=1}^{N} e^{i\mathbf{q}\cdot\mathbf{r}_j(0)}\frac{d}{dt}\langle e^{i\mathbf{q}\cdot\int_0^t du/\nu\ \boldsymbol{\xi}_j(u)}\rangle \qquad (27)$$

When $\boldsymbol{\xi}_j(t)$ is assumed to be a stationary and central Gaussian random process, then the average of exp$[i\mathbf{q}\cdot\int_0^t du/\nu\ \boldsymbol{\xi}_j(u)]$ is easily evaluated as

$$\langle e^{i\mathbf{q}\cdot(1/\nu)\int_0^t du\boldsymbol{\xi}_j(u)}\rangle = e^{-q^2D_S^St} \qquad (28)$$

so that

$$\langle n_{\mathbf{q}}(t)\rangle = -q^2D_S^{S}\varrho_{\mathbf{q}}(0)\, e^{-q^2D_S^St} \qquad (29)$$

where, we recall, $D_S^S = k_BT/\nu$. A similar calculation shows that

$$\langle n_{\mathbf{q}}(t)\, \varrho_{-\mathbf{q}}(0)\rangle = -q^2D_S^{S}|\varrho_{\mathbf{q}}(0)|^2e^{-q^2D_S^St} \qquad (30)$$

Note that $\langle\cdots\rangle$ implies only the average with respect to the realizations of the fastly fluctuating white noise $\boldsymbol{\xi}_j(t)$. The consecutive average with respect to the initial equilibrium distribution of particle positions leads to ($\mathbf{q} \neq 0$)

$$\langle\langle n_{\mathbf{q}}(t)\rangle\rangle = 0 \qquad (31)$$

and

$$\langle\langle n_{\mathbf{q}}(t)\, \varrho_{-\mathbf{q}}(0)\rangle\rangle = -q^2D_S^{S}\left(\frac{N}{\Omega^2}\right)e^{-q^2D_S^St} \qquad (32)$$

which demonstrates that the equality proposed in eq 25 is invalid even when the second average is performed. However, eq 31 remains valid also in case of interacting particles as can be seen from eq 21.

In order to demonstrate that these properties are indeed crucial in the calculation of the dynamic correlation functions, we start with eq 21 in the absence of interactions:

$$\dot{\varrho}_{\mathbf{q}}(t) = n_{\mathbf{q}}(t) \qquad (33)$$

By multiplying both sides by $\varrho_{-\mathbf{q}}(0)$ and using eq 32, we find

$$\frac{d}{dt}\langle\langle \varrho_{\mathbf{q}}(t)\, \varrho_{-\mathbf{q}}(0)\rangle\rangle = -q^2D_S^{S}\langle|\varrho_{\mathbf{q}}(0)|^2\rangle e^{-q^2D_S^St} \qquad (34)$$

which leads to the correct result

$$\langle\langle \varrho_{\mathbf{q}}(t)\, \varrho_{-\mathbf{q}}(0)\rangle\rangle = e^{-q^2D_S^St}\langle|\varrho_{\mathbf{q}}(0)|^2\rangle \qquad (35)$$

For noninteracting particles the static structure factor $\langle|\varrho_{\mathbf{q}}|^2\rangle$ is, of course, equal to N/Ω^2. Had one used the properties given in eq 25, one would be led to the nonphysical conclusion that $\langle\langle \varrho_{\mathbf{q}}(t)\, \varrho_{-\mathbf{q}}(0)\rangle\rangle$ does not relax at all.

Although it is a trivial case, we now consider the interdiffusion process in a two-component suspension of noninteracting particles with Stokesian friction coefficients ν_A and ν_B. The starting equations are

$$\dot{\varrho}_{\mathbf{q}}^{\alpha} = n_{\mathbf{q}}^{\alpha}(t) \qquad (36)$$

$$n_{\mathbf{q}}^{\alpha}(t) = \frac{1}{\Omega}\sum_{j=1}^{N_\alpha} i\mathbf{q}\cdot\boldsymbol{\xi}_j^{\alpha}(t)\, e^{i\mathbf{q}\cdot\mathbf{r}_j^{\alpha}(t)} \qquad (37)$$

with

$$\langle\boldsymbol{\xi}_j^{\alpha}(t)\, \boldsymbol{\xi}_k^{\beta}(t')^T\rangle = 2k_B T\mathbf{1}\delta_{jk}\delta_{\alpha\beta}\delta(t-t') \qquad (38)$$

and $\alpha, \beta \in \{A,B\}$.

The interdiffusion coefficient can be calculated from the first cumulant of the dynamic correlation function of the composition fluctuation. The latter is defined in linear approximation as

$$C_{\mathbf{q}}(t) = \frac{\varrho_{\mathbf{q}}^{A}(t)}{\bar{\varrho}_A} - \frac{\varrho_{\mathbf{q}}^{B}(t)}{\bar{\varrho}_B} \qquad (39)$$

where $\bar{\varrho}_\alpha = N_\alpha/\Omega$ denotes the uniform densities of the components. The stochastic evolution equation for $C_{\mathbf{q}}(t)$ follows from eqs 36–38 as

$$\dot{C}_{\mathbf{q}}(t) = \frac{n_{\mathbf{q}}^{A}(t)}{\bar{\varrho}_{A}} - \frac{n_{\mathbf{q}}^{B}(t)}{\bar{\varrho}_{B}} \qquad (40)$$

Multiplying both sides by $C_{-\mathbf{q}}(0)$, averaging, and making use of eq 32 to calculate $\langle\langle n_{\mathbf{q}}^{\alpha}(t) C_{-\mathbf{q}}(0)\rangle\rangle$, one finds

$$\frac{d}{dt}\langle\langle C_{\mathbf{q}}(t)\, C_{-\mathbf{q}}(0)\rangle\rangle = -q^{2} \sum_{\alpha=A,B} D_{S\alpha}{}^{S} \frac{\langle|\varrho_{\mathbf{q}}{}^{\alpha}|^{2}\rangle}{\bar{\varrho}_{\alpha}{}^{2}} e^{-q^{2} D_{S\alpha}{}^{S} t} \qquad (41)$$

where $D_{S\alpha}{}^{S} = k_{B}T/\nu_{\alpha}$ are the short-time tracer-diffusion coefficients of the components. The interdiffusion coefficient is defined by

$$D_{\mathrm{int}} = -\lim_{t\to 0}\lim_{q\to 0} \frac{1}{q^{2}} \frac{d}{dt} \ln \langle\langle C_{\mathbf{q}}(t)\, C_{-\mathbf{q}}(0)\rangle\rangle \qquad (42)$$

This definition of the interdiffusion coefficient is not affected when $C_{\mathbf{q}}(t)$ is redefined by a multiplicative constant. Notice also that, in case of solutions of interacting particles, one needs to distinguish between the definitions of long-time and short-time interdiffusion coefficients, $D_{\mathrm{int}}{}^{S}$ and $D_{\mathrm{int}}{}^{L}$. Formally, the definitions both of $D_{\mathrm{int}}{}^{S}$ and $D_{\mathrm{int}}{}^{L}$ are given by eq 42. However, in defining $D_{\mathrm{int}}{}^{L}$ it is understood that the hydrodynamic limit of $\langle\langle C_{\mathbf{q}}(t)\, C_{-\mathbf{q}}(0)\rangle\rangle$ is substituted on the right-hand side of eq 42.

Substituting $\langle\langle \dot{C}_{\mathbf{q}}(t)\, C_{-\mathbf{q}}(0)\rangle\rangle$ from eq 41, we find

$$D_{\mathrm{int}} = \left[\frac{\langle|\varrho_{\mathbf{q}}{}^{A}|^{2}\rangle}{\bar{\varrho}_{A}{}^{2}} D_{SA}{}^{S} + \frac{\langle|\varrho_{\mathbf{q}}{}^{B}|^{2}\rangle}{\bar{\varrho}_{B}{}^{2}} D_{SB}{}^{S}\right] \Big/ \langle|C_{\mathbf{q}}|^{2}\rangle \qquad (43)$$

Since $\langle|\varrho_{\mathbf{q}}{}^{\alpha}|^{2}\rangle/\bar{\varrho}_{\alpha}{}^{2} = 1/N_{\alpha}$ and $\langle|C_{\mathbf{q}}|^{2}\rangle = 1/N_{A} + 1/N_{B}$ for noninteracting particles, eq 43 reduces to the well-known result

$$D_{\mathrm{int}} = \phi_{B} D_{SA}{}^{S} + \phi_{A} D_{SB}{}^{S} \qquad (44)$$

Here, $\phi_{\alpha} = N_{\alpha}/N$, $N = N_{A} + N_{B}$, and equal partial molar volumes of both components are implied. The result (44) is consistent with the fast mode theory. When the friction coefficients ν_{A} and ν_{B} are the same, the interdiffusion coefficient is identical to the self-diffusion coefficient $D_{S}{}^{S}$ in noninteracting systems. This result is true also in the case of interacting particles, provided the interaction potentials between particle pairs, i.e., V^{AA}, V^{BB}, and V^{AB} are the same. This is the case, for example, in a partially colored molecular fluid or suspension which is considered to be a binary mixture of colored and uncolored particles. In binary suspensions of colored but otherwise identical particles it is found that $D_{\mathrm{int}}{}^{S} = D_{S}{}^{S}$ and $D_{\mathrm{int}}{}^{L} = D_{S}{}^{L}$. The fact that $D_{\mathrm{int}} = D_{S}$ in such systems is well documented in the literature.[1-3] Although well-known, we reproduced these results here using the same procedure followed in the B theory in order to make the following point: The expression of the interdiffusion coefficient obtained in the B theory (eq 15 of ref 5) violates the above conclusion, because it yields $D_{\mathrm{int}} = 0$, when the interaction potentials between particle pairs are identical, i.e., $\epsilon_{AA} = \epsilon_{BB} = \epsilon_{AB}$ in the notation of ref 5. This result would imply that the colored and uncolored components of a fluid do not mix. It seems that this nonphysical conclusion is reached as a consequence of the way the statistical properties of the multiplicative stochastic term $n_{\mathbf{q}}(t)$ in eq 23 are treated.

3. Conclusions

In light of the above discussions and demonstrative examples, it appears that the expression of the interdiffusion coefficient in a binary melt, proposed in the B theory, lacks theoretical support. On the other hand, the ANK result is based on the dynamic random-phase approximation in a ternary incompressible polymer mixture. The use of RPA in such mixtures is justified for the long chain limit. In the ANK theory, the RPA is extended to compressible binary mixtures by treating the latter as incompressible ternary mixtures, in which the third component is taken to be vacancies. This procedure may be questionable in a quantitative analysis of interdiffusion but it does not lead to inconsistencies when qualitative features are involved. In this procedure, one assigns a tracer-diffusion coefficient (D_{C} in eq 3) to vacancies, and this may be considered as an ill-defined concept. However, since the motion of vacancies is caused by the diffusion of the monomers, it is reasonable to express D_{C} as an appropriately weighted average of the tracer-diffusion coefficients D_{A} and D_{B} of the components, for example, as $D_{C} = \phi_{A}D_{A} + \phi_{B}D_{B}$. This procedure may remove the ambiguity associated with the dynamics of vacancies. The other possibility is to treat $\phi_{C}D_{C}$ as an adjustable parameter in the interpretation of an experiment, as was done by Feng et al.[6] in their study of the molecular weight dependence of interdiffusion.

In conclusion, we think that only the ANK theory, at present, provides an interpolation formula between the fast and slow mode results for the interdiffusion coefficient, which has some justification.

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References and Notes

(1) Hess, W.; Nägele, G.; Akcasu, A. Z. *J. Polym. Sci.* **1990**, *B28*, 2233.
(2) Akcasu, A. Z.; Nägele, G.; Klein, R. *Macromolecules* **1991**, *24*, 4408.
(3) Kehr, K. W.; Binder, K.; Reulin, S. M. *Phys. Rev. B* **1989**, *39*, 4891.
(4) Binder, K.; Jilge, W.; Carmesin, I.; Kremer, K. *Macromolecules* **1990**, *23*, 5001.
(5) Brereton, M. P. *Prog. Colloid Polym. Sci.* **1993**, *91*, 8.
(6) Feng, Y.; Han, C. C.; Takenaka, M.; Hashimoto, T. *Polymer* **1992**, *33*, 2719.
(7) Meier, G.; Fytas, G.; Momper, B.; Fleicher, G. *Macromolecules* **1993**, *26*, 5310.
(8) Fox, R. *Phys. Rep.* **1978**, *48*, 179.
(9) Hanna, S. N.; Hess, W.; Klein, R. *Physica A* **1982**, *111*, 181.

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