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The interdiffusion coefficient in two-component polymeric mixtures

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1. Introduction.

The interdiffusion process in two- or multi-component liquids has attracted increasing attention in recent years. One reason for the interest in this subject is its pertinence to spinodal decomposition [1-4] which is one of the most active research fields in non-equilibrium statistical mechanics. Another reason is a better theoretical understanding of the interdiffusion process needed for the interpretation of the recent experiments on polymeric mixtures [5-8], in which the interdiffusion coefficient is measured with higher accuracy by the novel advanced experimental techniques. In high-molecular weight polymeric mixtures the interdiffusion is so slow that it can be observed in macroscopic time scales. Needless to say that such a slow mixing of components has important consequences in the processing of polymeric materials.

Theoretically, the interdiffusion coefficient has been calculated either in a purely phenomenological way, using the methods of irreversible thermodynamics, or by the application of the dynamic random phase approximation. Both kinds of approaches should be equally suited for the treatment of long-wavelength macroscopic modes. So it is surprising that the outcome of these works is quite different. One result, which is known as Hartley-Crank equation, writes [5, 9, 10].

\[
D = (X_B P_A D_A + X_A P_B D_B) \frac{Q}{Q},
\]

where \(X_{A,B}\) are the fractions of A or B molecules, \(P_{A,B}\) are the polymerization indices and \(D_{A,B}\) are their diffusivities. \(Q\) is a thermodynamic factor. The other results, derived by means of the RPA [1, 2, 11], or by introducing vacancies as dynamical variables in an irreversible thermodynamics approach [3, 4], is

\[
D = \left[ \frac{X_B}{P_A D_A} + \frac{X_A}{P_B D_B} \right]^{-1} \frac{Q}{Q}.
\]

The thermodynamic factor \(Q\) is the same as above, but with respect to the kinetic factor, both formulas are completely different. This can be seen at its best when we consider the case where \(D_A \gg D_B\). Then, according to equation (1.1), \(D \sim D_A\), but from equation (1.2) one would obtain \(D \sim D_B\). So the open question is, is the interdiffusion process dominated by the slow, or by the fast component? Only in the limit where the concentration of one of the
species vanishes, both formulas above agree. For $X_A \to 0$, $X_B = 1 - X_A \to 1$, one obtains $D = D_A$, since in this limit $Q = 1/p_A$. This also shows that the diffusivities which are used here, are not the self-diffusion coefficients of the unmixed components, but are related to the tracerdiffusion coefficients of a molecule of the one kind, immersed in a system which otherwise consists only of particles of the other kind.

Our own work here cannot give a definite answer to the controversy addressed above. But because of the practical importance of this problem, it seemed worthwhile to us to present a rigorous microscopic formulation of the interdiffusion coefficient in a binary liquid. This can serve as a sound basis for the discussion of various approximations, which may lead either to the Hartley-Crank equation (1.1), or to de Gennes’ result (1.2).

2. Theoretical background.

We consider a set of dynamical variables $A = \{p_A, p_B, J_A, J_B\} = \{p, J\}$, where $A$ and $B$ are the two species of polymers and $p_i$ and $J_i$ $(i = A, B)$ are Fourier transforms of the local concentration fluctuations and of fluctuations in the longitudinal currents,

$$
\rho_i = \sum_{m=1}^{N_i} \sum_{a=1}^{p_i} e^{i k \cdot r_m^a} \tag{2.1}
$$

$$
J_i = \sum_{m=1}^{N_i} \sum_{a=1}^{p_i} v_m^a e^{i k \cdot r_m^a} \tag{2.2}
$$

$v_m^a = k \cdot v_m^a / |k|$ is the longitudinal velocity component of segment $(m, a)$. $p_i$ is the polymerization index and $N_i$ is the total number of polymers of species $i$. Let us assume a perturbed initial distribution $\psi(0)$ which does not deviate appreciably from the equilibrium distribution $\psi_{eq}$. According to Zwanzig-Mori [12, 13] projection operator formalism the mean values of $\rho(t)$ and $J(t)$ with respect to $\psi(0)$ satisfy the following set of equations:

$$
\dot{\rho}(t) = i k \tilde{\rho}(t) \tag{2.3}
$$

$$
\dot{\tilde{J}}(t) = i k \langle JJ^+ \rangle \cdot \langle pp^+ \rangle^{-1} \cdot \tilde{J}(t) - \int_0^t du \xi(t-u) \cdot \tilde{J}(u) \tag{2.4}
$$

where $\rho(t) = \langle \rho(t) \rangle_{\psi(0)}$ and $J(t) = \langle J(t) \rangle_{\psi(0)}$. To simplify the notation, we shall not distinguish between $\rho(t)$ and $J(t)$, which are functions of particle coordinates and momenta, and the averages $\bar{\rho}(t)$ and $\bar{J}(t)$, in the following. The elements of the static structur factor $\langle \rho_i \rho_j^+ \rangle$ are defined as

$$
\langle \rho_i \rho_j^+ \rangle = \sqrt{N_i p_i^2 N_j p_j^2} S_{ij} \tag{2.5}
$$

where

$$
S_{ij} = S_{ij}^S \delta_{ij} + \sqrt{N_i p_i N_j p_j} S_{ij}^{INT} \tag{2.6}
$$

$S_{ij}^S$ is the single-chain structure factor or form factor defined by

$$
S_{ij}^S = \frac{1}{N_i p_i N_j p_j} \sum_{m=1}^{N_i} \sum_{a=1}^{p_i} \sum_{\beta=1}^{p_j} \langle e^{i k \cdot (r_m^a - r_\beta^j)} \rangle \tag{2.7}
$$

and the interference structure factor $S_{ij}^{INT}$ is defined by

$$
S_{ij}^{INT} = \frac{1}{N_i p_i N_j p_j} \sum_{m=1}^{N_i} \sum_{a=1}^{p_i} \sum_{\beta=1}^{p_j} \sum_{\alpha=1}^{p_i} \sum_{\gamma=1}^{p_j} \times \langle e^{i k \cdot (r_m^a - r_\beta^j)} \rangle \tag{2.8}
$$

The static current correlation matrix is

$$
\langle JJ^+ \rangle = k_B T \begin{bmatrix} N_A p_A & 0 \\ 0 & N_B p_B \\
\frac{m_A}{m_B} & \frac{m_B}{m_A} \end{bmatrix} \tag{2.9}
$$

The small-k limit of the memory matrix is

$$
\xi(k \to 0, t) = \frac{\beta}{N_A p_A N_B p_B} \langle F_{AB}(t) F_{AB}(0) \rangle \times \begin{bmatrix} 1 & \frac{m_B}{m_A} & \frac{1}{M_A} \\ -\frac{m_A}{m_B} & \frac{1}{m_A} & \frac{1}{M_B} \end{bmatrix} , \tag{2.10}
$$

where $M_i = m_i N_i p_i$ denotes the total mass and $m_i$ the mass of one segment in the $i$-th component. $\xi(t)$ is the normalized autocorrelation function of forces between the two species $A$ and $B$,

$$
\xi(t) = \frac{\beta}{N_A p_A N_B p_B} \langle F_{AB}(t) F_{AB}(0) \rangle \cdot \left( \beta = \frac{1}{k_B T} \right) . \tag{2.11}
$$

For later use we denote the longitudinal component of the interaction forces between two segments $(m, a)$ and $(n, \beta)$ as $f_{mm}^{ab}(t)$. Then the force between two polymers $m$ and $n$ is

$$
f_{mm}^{ab}(t) = \sum_{a=1}^{p_i} \sum_{\beta=1}^{p_j} f_{m\beta}^{ab}(t) , \tag{2.12}
$$

if $m$ belongs to species $i$ and $n$ belongs to species $j$. The total force between the two species is

$$
F_{AB}(t) = \sum_{m=1}^{N_a} \sum_{n=1}^{N_b} f_{mm}^{ab}(t) = \sum_{m=1}^{N_a} \sum_{n=1}^{N_b} \sum_{a=1}^{p_A} \sum_{\beta=1}^{p_B} f_{m\beta}^{ab}(t) . \tag{2.13}
$$
It is important to note that the memory function $\xi(t)$ does not develop with the full time evolution operator, but only with a time evolution operator acting in the subspace of variables orthogonal to the set $A$.

The diffusion equation for $\rho(t)$ can be obtained if we consider the case where the mean of the initial value of the currents with respect to $\psi(0)$ is zero, $J(0) = \langle J(0) \rangle \neq 0$. This initial condition would be indeed appropriate for diffusion experiments, which measure only directly the densities $\rho_j(t)$. Then a first integral of equation (2.4), together with equation (2.3) yields

$$
\rho(t) = -k^2 \int_0^t du \Delta(t - u) \cdot \langle \rho \rho^+ \rangle^{-1} \cdot \rho(u),
$$

(2.14)

where the matrix $\Delta(t)$ is to be determined by the equation

$$
\Delta(t) = -\int_0^t du \xi(t - u) \cdot \Delta(u)
$$

(2.15)

and the initial condition $\Delta(0) = \langle JJ^+ \rangle$.

In the long-wavelength limit it can be shown with the help of equation (2.4) that

$$
\lim_{k \to 0} \Delta(t) = \lim_{k \to 0} \langle J(t) J^+(0) \rangle,
$$

(2.16)

where $J(t)$ evolves in time with respect to the regular propagator $\exp(\tau L)$. If a Markov limit, $k \to 0, t \to \infty$ with $k^2 t$ is fixed, is allowed, equation (2.14) is reduced to an ordinary diffusion equation,

$$
\rho(t) = -k^2 \mathcal{D} \cdot \rho(t),
$$

(2.17)

where the diffusion matrix is given by the Kubo formula

$$
\mathcal{D} = \lim_{k \to 0} \int_0^\infty d\tau \langle J(t) J^+(0) \rangle \cdot \langle \rho \rho^+ \rangle^{-1}.
$$

(2.18)

Although it is often used as a starting point in the phenomenological description of diffusion in fluid mixtures [3-5, 9, 10], the diffusion equation (2.17) is meaningful only when the Markov limit exists, i.e., if the time integral over the current autocorrelation function in equation (2.18) is finite.

But from equation (2.10) it is obvious that the small-$k$ limit of the matrix $\xi(k)$ becomes singular. As a consequence of equation (2.15), also the $\Delta$-matrix is singular for $k \to 0$ and a diffusion equation, like equation (2.17), cannot be written down for the coupled set of densities $\rho_A(t)$ and $\rho_B(t)$. Often one can read the statement that this singularity of the diffusion matrix is a result of the incompressibility of the liquid. But our detailed derivation makes clear that this is not true. No assumption of incompressibility has been introduced so far. The physical origin for this singular behavior is of course the conservation of the total momentum of the fluid. Since the total momentum is undamped, the time integral in the Kubo-relation, equation (2.12), does not converge and the proposed Markov limit does not exist. Nevertheless, in many papers on diffusion in polymeric mixtures one finds equations like (2.17) in use.

3. Density fluctuations and interdiffusion.

The singularity of the $\alpha$ or diffusion-matrix can be resolved by considering instead of $\rho_A(t)$ and $\rho_B(t)$ directly linear combinations as the dynamical variables. Formally this is done by a transformation matrix $\mathcal{R}$,

$$
\rho' = \mathcal{R} \cdot \rho.
$$

(3.1)

The new friction matrix then is

$$
\xi' = \mathcal{R} \cdot \xi \cdot \mathcal{R}^{-1}.
$$

(3.2)

It is possible to choose $\mathcal{R}$ in such a way that the transformed matrix $\xi'$, in the case of two-component fluid, has the following form

$$
\xi'(k, t) = \begin{bmatrix} 0 & 0 \\ 0 & Z \end{bmatrix} \xi(k, t) + k^2 \eta(k, t),
$$

(3.3)

where $Z$ is a constant to be determined. The matrix $\eta(k, t)$ includes thermal and viscous processes in the fluid. It is assumed that the small-$k$ limit of $\eta(k, t)$ is finite for a fluid.

Using the small-$k$ limit of $\xi(k, t)$, given equation (2.10) in equations (3.2) and (3.3), one finds

$$
\mathcal{R} = \begin{bmatrix} m_A/M & m_B/M \\ 1/N_A P_A & -1/N_B P_B \end{bmatrix},
$$

(3.4)

where $M = M_A + M_B$ denotes the total mass of the fluid. The value of $Z$ is obtained as

$$
Z = \frac{M}{m_A m_B}.
$$

(3.5)

This value of $Z$ is unique. However, the rows of the matrix $\mathcal{R}$ can be multiplied by two separate factors. Let us denote the components of $\rho'$ by $\rho_+$ and $\rho_-$. Then the above transformation implies

$$
\rho_+ = \frac{1}{M} [m_A \rho_A + m_B \rho_B],
$$

(3.6a)

$$
\rho_- = \frac{1}{N_A P_A} \rho_A - \frac{1}{N_B P_B} \rho_B.
$$

(3.6b)

The dynamical variable $\rho_+$ denotes the relative,
total mass density in the $k$-space. The associated current density

$$ J_+ = \frac{1}{M} [m_A J_A + m_B J_B] \quad (3.7) $$

is the total momentum current density. We note that $\rho_+ = 1$ when $k = 0$ as a result of our choice of the arbitrary factor in the first row of $R$. When $k = 0$, we have

$$ J_+ = \frac{m_A V_A + m_B V_B}{M} \quad (3.8a) $$

with

$$ V_i = \sum_{\alpha=1}^{N_i} \sum_{\alpha=1}^{n_i} v_{\alpha}^m. \quad (3.8b) $$

Hence, $J_+ = 0$ in the small-$k$ limit, which explains the form of $\xi^t(t)$ given in equation (3.3) in this limit.

The second dynamical variable $\rho_-$ represents the difference between the normalized local densities $\rho_A/N_A p_A$ and $\rho_B/N_B p_B$ of the components. To lowest order in the density fluctuations, the variable $\rho_-$ is directly related to the local concentration of the two components,

$$ c_A(r, t) = \frac{\rho_A(r, t)}{\rho_A(r, t) + \rho_B(r, t)} = 1 - c_B(r, t). \quad (3.9) $$

Expanding the $\rho_i$ around their mean values $N_i p_i/V_i$, one obtains, e.g.

$$ c_A(r, t) = X_A + X_A X_B \rho_-(r, t), \quad (3.10) $$

with $X_i = N_i p_i/(N_A p_A + N_B p_B)$ the fraction of segments of kind $i$. The long-wavelength limit of the variable $\rho_-$ is zero, $\lim_{k \to 0} \rho_-(k, t) = 0$.

The associated current density is

$$ J_- = J_A - J_B \quad (3.11) $$

Its meaning becomes clearer when $k = 0$: $J_- = V_A/N_A p_A - V_B/N_B p_B$ which is the relative velocity of the center of masses of the two components. In contrast to $J_+$, $J_-$ is not conserved.

In order to write down the equations for $\rho_+$ and $\rho_-$, we need $\langle J' J'^+ \rangle$ and $\langle \rho' \rho'^+ \rangle$ in equation (2.4):

$$ \langle J' J'^+ \rangle = R \cdot \langle JJ^+ \rangle \cdot R^T $$

$$ = k_B T \begin{bmatrix} 1/M & 0 \\ 0 & 1/\mu \end{bmatrix} \quad (3.12a) $$

where $\mu$ is a reduced mass defined by

$$ \frac{1}{\mu} = \frac{1}{M_A} + \frac{1}{M_B}. \quad (3.12b) $$

The static correlation matrix $\langle \rho' \rho'^+ \rangle$ can be calculated directly using the components of $\rho'$ given in equations (3.6). It can also be calculated using

$$ \langle \rho' \rho'^+ \rangle = R \cdot \langle \rho \rho^+ \rangle \cdot R^T. $$

This form is particularly convenient to calculate the determinant of $\langle \rho' \rho'^+ \rangle$ as

$$ \Delta = \det \langle \rho' \rho'^+ \rangle = \frac{1}{N_A p_A N_B p_B} [S_{AA} S_{BB} - S_{AB}^2]. \quad (3.13) $$

The transformed equation of motion reads:

$$ \rho'(t) = -k^2 \langle J' J'^+ \rangle \cdot \langle \rho' \rho'^+ \rangle \cdot \rho'(t) $$

$$ - \int_0^t du \begin{bmatrix} 0 & 0 \\ 0 & \xi(t-u) \end{bmatrix} \cdot \rho'(u) $$

$$ - k^2 \int_0^t du \frac{\eta(k, t-u) \cdot \rho(u)}{\rho_-(k, t)}. \quad (3.14) $$

Except for linearization, this equation is still exact for the time evolution of $\rho_+(t)$ and $\rho_-(t)$, and for any $k$. We are however interested in its small-$k$ limit. In this limit, we shall neglect the last term, primarily for simplicity in presenting our main point. The physical implication of this approximation will be discussed later whenever the occasion arises. Hence, in the small-$k$ limit we obtain

$$ \rho_+(t) = -k^2 k_B T \begin{bmatrix} 1/M & 0 \\ 0 & 1/\mu \end{bmatrix} \begin{bmatrix} \rho_+ \rho_+ \rho_+ \rho_+ \\ \rho_+ \rho_+ \rho_+ \rho_+ \end{bmatrix} \rho_+(t) $$

$$ - \frac{\langle \rho' \rho'^+ \rangle}{\Delta} \rho_+(t) \quad (3.15a) $$

$$ \rho_-(t) = -k^2 k_B T \mu \times $$

$$ \times \left[ - \frac{\langle \rho_\rho^+ \rangle}{\Delta} \rho_+(t) + \frac{\langle \rho_\rho^+ \rangle}{\Delta} \rho_-(t) \right] $$

$$ - \frac{M}{M_A M_B} \int_0^t du \xi(t-u) \rho_-(u). \quad (3.15b) $$

These equations are the starting equations in our approach to the dynamics of two-component fluids in the small-$k$ limit.

The first observation is that the equation $\dot{\rho}_+(t)$ does not contain the first time-derivative $\dot{\rho}_+(t)$. The physical implication of this fact can be understood in terms of the dispersion relation for the coupled system:
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\[ \begin{align*}
\left[ s^2 + k^2 \frac{k_B T}{M} \frac{\langle \rho_- \rho_+ \rangle}{\Delta} \right] & \times \\
\left[ s^2 + s \frac{M}{m_A m_B} \xi(s) + k^2 \frac{k_B T}{\mu} \frac{\langle \rho_+ \rho_+ \rangle}{\Delta} \right] = \\
& = k^4 \left( \frac{k_B T}{M} \right)^2 \left( \frac{\rho_- \rho_+^*}{\Delta^2} \right)^2,
\end{align*} \]

(3.16)

\( \xi(s) \) is the Laplace-transform of the friction function.

The right hand side of this equation represents the coupling between the natural modes of the system, characterized by the two factors on the left-hand side. The first factor represents two undamped sound modes propagating in the two opposite directions with a speed

\[ c_L^2 = \frac{k_B T}{M} \frac{\langle \rho_- \rho_+ \rangle}{\Delta}. \]

(3.17)

These modes correspond to the two roots \( s_{1,2} = \pm ikc_L \), and describe the variation of \( \rho_+ (t) \) in time.

The reason why these modes are undamped is the neglect of \( \eta(0, t) \) in equation (3.15) in the small-\( k \) limit. However, they become damped when the coupling on the right hand side of equation (3.16) is taken into account.

The second bracket on the left hand side of equation (3.19) represents, in the small-\( s \) limit where \( \xi(s) \) can be approximated by \( \xi(0) \), a second order over-damped system with two real and negative roots:

\[ s_1 = -\frac{M}{m_A m_B} \xi(0) \]

(3.18a)

and

\[ s_2 = -k^2 \frac{k_B T}{\xi(0) N_A P_A N_B P_B} \frac{1}{\Delta}. \]

(3.18b)

These roots correspond, respectively, to momentum relaxation, and interdiffusion of the two components of the fluid. The presence of the coupling between these modes modifies the values of the roots of the dispersion relation as we discuss below. The modes characterized by equations (3.18) describe the relaxation of the fluctuations in \( \rho_+ (t) \) in time.

A closed diffusion equation for \( \rho_- (t) \) is obtained if the period of the sound mode \( 2 \pi /kc_L \), is much shorter than the diffusional relaxation time \( 1/s_2 \) given in equation (3.18b). This is the case if the liquid can be treated as incompressible, e.g. Then

\[ \rho_A (t) = -\rho_B (t), \]

(3.19)

assuming that the segments in both components have equal volumes, and

\[ \rho_+ (t) = \frac{m_A - m_B}{M} \rho_A (t) \]

(3.20a)

For the incompressible system the determinant \( \Delta \) is zero, leading to an infinite velocity of sound \( c_L \). It can be shown that equations (3.20) are equivalent with the equation

\[ \rho_+ (t) = \frac{\rho_+ \rho_+^*}{\rho_- \rho_-^*} \rho_- (t). \]

(3.21)

When this relation is substituted into equation (3.15(b)), a closed equation is obtained for \( \rho_- (t) \)

\[ \rho_- (t) = -k^2 \frac{k_B T}{\mu} \frac{1}{\rho_- \rho_-^*} \rho_- (t) \]

\[ -M \frac{m_A m_B}{\rho_-} \int_0^t du \xi(t-u) \rho_- (u). \]

(3.22)

In the Markov limit, this leads to a diffusion equation

\[ \dot{\rho}_- (t) = D \nabla^2 \rho_- (t) \]

(3.23)

with an interdiffusion coefficient

\[ D = \frac{k_B T}{\xi(0) N_A P_A N_B P_B} \frac{1}{\rho_- \rho_-^*} = \Lambda \frac{1}{\rho_- \rho_-^*}. \]

(3.24)

One can show (cf. Eq. (2.14)) that the Onsager coefficient \( \Lambda \) can also be written as

\[ \Lambda = \lim_{k \to 0} \int_0^\infty dr \langle J_- (t) J_-^* (0) \rangle. \]

(3.25)

We note again that the time dependence of \( J_- (t) \) in equation (3.22) is governed by the regular propagator \( \exp (itL) \), whereas that of \( \xi(s) \) in equation (3.20) is governed by the modified propagator \( \exp (it(1-P)L) \). The important point is that, whereas the friction matrix as a whole was found to be singular in the limit \( k \to 0 \), there is no reason to assume that the friction function \( \xi(s) \), as defined in equation (2.11), does not behave regular in the limit \( s \to 0 \). As a consequence, although the time-integral over the correlation functions of the current components in equation (2.18) is divergent, the time-integral of the autocorrelation function of the special linear combination \( J_- (t) \) in equation (3.25) will be convergent.

With the definition of a thermodynamic factor \( Q \) as

\[ Q = \left( \frac{1}{N_A P_A} + \frac{1}{N_B P_B} \right) \langle \rho_- \rho_-^* \rangle^{-1} \]

\[ = \frac{X_B}{P_A S_{AA}} = \frac{X_A}{P_B S_{BB}} \]

(3.26)
for the incompressible system, equations (3.20), the interdiffusion coefficient can be written in the compact form

\[
D = \frac{k_B T}{(N_A p_A + N_B p_B)} \xi(0) Q
= \left( \frac{1}{N_A p_A} + \frac{1}{N_B p_B} \right)^{-1} \Lambda Q .
\]  

(3.27)

This result for the interdiffusion coefficient is of course well known. The actual value of our derivation lies in the precise definition of the relevant friction coefficient

\[
\xi(0) = \int_0^\infty dt \xi(t) = \frac{\beta}{N_A p_A N_B p_B} \times \int_0^\infty dt \langle F_{AB}(t) F_{AB}(0) \rangle
\]  

(3.28)

as the normalized time integral over the correlation function of the total force between the two subsystems.

4. Two special cases.

4.1 A MIXTURE OF LABELLED MOLECULES. — As an illustration of the foregoing discussions, we now consider a special case in which « A » and « B » components are dynamically identical, and « A » and « B » polymers have the same polymerization degree, \( p_A = p_B = p \), and the same mass per segment, \( m_A = m_B = m \). We imagine that \( N_A \) polymers of a one-component fluid are colored or labelled. In this case correlations between pairs of \( A, A \) molecules, \( B, B \) molecules and \( A, B \) molecules are identical. The following results are self-explanatory:

\[
S_{AA} = 1 + (N_A/N_B)^{1/2} S_{AB}
\]

\[
S_{BB} = 1 + (N_B/N_A)^{1/2} S_{AB}
\]

\[
S_{AB} = (N_A N_B)^{1/2} [S - 1]/N
\]

(4.1a)

(4.1b)

(4.1c)

where \( S = S(0) \) is the total static structure factor in the small-\( k \) limit, of the one-component fluid. The variables \( \rho_+ \) and \( \rho_- \) are related to \( \rho_A \) and \( \rho_B \) by

\[
\rho_+ = \frac{1}{N p} [\rho_A + \rho_B]
\]

\[
\rho_- = \frac{\rho_A}{N_A p} - \frac{\rho_B}{N_B p}
\]

so that

\[
\langle \rho^t \rho^s \rangle = \begin{bmatrix} S/N & 0 \\ 0 & \frac{N}{N_A N_B} \end{bmatrix}.
\]

The fact that this matrix is diagonal implies that there is no direct coupling between the sound modes and diffusive modes. The equations (3.15) reduce then to

\[
\dot{\rho}_+(t) = -\frac{k_B T}{m p S(0)} \rho_+(t) \quad \text{(4.2a)}
\]

\[
\dot{\rho}_-(t) = -\frac{k_B T}{m p} \rho_-(t) - \frac{N p}{m} \times \int_0^t du \xi(t-u) \dot{\rho}_-(u) . \quad \text{(4.2b)}
\]

The first equation corresponds to sound propagation in a one-component fluid with the conventional definition of speed of sound. The sound waves do not differentiate between « A » and « B » components. Again, the absence of the damping of the sound modes is due to the simplification we introduced by keeping only the first term in the expansion of the memory function in powers of \( k^2 \) (cf. Eq. (3.14)). The equation (4.2b) defines the following interdiffusion coefficient in the Markov limit:

\[
D = \frac{k_B T}{N p^2 \xi(0)} .
\]

(4.3)

In the limit when there is only one colored particle, this situation corresponds to self-diffusion and then the interdiffusion coefficient just becomes the self-diffusion coefficient in a one-component fluid,

\[
D_s = k_B T/(p \xi_s) ,
\]

(4.4)

where now \( \xi_s \) is the friction coefficient per segment, defined here as

\[
\xi_s = N p \xi(0)
\]

\[
= \frac{\beta}{P} \int_0^\infty dt \langle F_{AB}(t) F_{AB}(0) \rangle ,
\]

(4.5)

according to equation (2.11). Now \( F_{AB} \) is the force of all other polymers on one test-polymer.

4.2 POLYMERS IN A LOW-MOLECULAR WEIGHT SOLVENT. — Low-molecular weight liquids can be easily incorporated in the theory presented here if we set the respective polymerization degree \( p_i = 1 \). Of special interest is the case of a polymer solution, which corresponds to the condition \( p_A \gg 1, p_B = 1 \). It is instructive to consider the structure and the physical meaning of the friction function for this situation. From equations (3.28) and (2.13)

\[
\tilde{\xi}(0) = \frac{\beta}{N_B N_A p_A} \sum_{a=1}^{N_A} \sum_{b=1}^{N_B} \int_0^\infty dt \times \times \sum_{s,t=1}^{N_B} \langle f_{ab}^{m_s}(t) f_{ab}^{m_t}(0) \rangle
\]

\[
= \frac{1}{N_B N_A p_A} \sum_{a=1}^{N_A} \sum_{b=1}^{N_B} \langle \xi_{a_b}^{m_s} \rangle
\]

(4.6)
if we define a two-segment friction matrix with elements
\[ \xi_{\alpha\beta}^{mn} = \beta \sum_{s, r = 1}^{N_B} \int_0^\infty \langle f_a^m(t) f_b^n(0) \rangle_{A} \Delta_{\alpha\beta}. \]  
(4.7)

Here \( \langle \cdots \rangle_{A} \) is a conditional average over the solvent degrees of freedom, subject to a fixed distribution of polymer segments. This way to express the friction coefficient allows to make contact with the traditional approaches to polymer solution dynamics, the Kirkwood-Riseman theory [15] e.g., in which the solvent is treated phenomenologically as a hydrodynamic continuum. One can show [14] that the \( \xi_{\alpha\beta}^{mn} \), defined as in equation (4.7) gives the response of the solvent friction force on a segment \((m, \alpha)\), due to the motion of segment \((n, \beta)\). The non-diagonal elements of this friction matrix describes therefore hydrodynamic interaction between two segments. Usually the effect of hydrodynamic interaction is represented in terms of two-segment mobilities instead of two-segment friction coefficients. This is more convenient since for the two-segment mobilities an explicit expression can be given, the Oseen-tensor [15]. The mobilities are related to the friction coefficients (4.7) by the matrix equation

\[ \sum_{n=1}^{N_A} \sum_{\beta=1}^{P_A} \mu_{n\beta}^{mn} \xi_{\beta\gamma}^{n\pi} = k_B T \delta_{\gamma\alpha} \delta_{mn}. \]  
(4.8)

The interdiffusion coefficient for the case of a polymer solution is then (using Eqs. (3.26) and (3.27))

\[ D = \frac{X_B^2 k_B T}{p_A S_{AA} \xi_4(p_A, X_A)}, \]  
(4.9)

with the friction coefficient per segment

\[ \xi_4 = \frac{1}{N_A p_A} \sum_{n=1}^{N_A} \sum_{\beta=1}^{P_A} \langle \xi_{nm}^{m\pi} \rangle, \]  
(4.10)

which is in general a function of polymer concentration as well as of polymerization degree. Especially for a dilute solution, \( X_B = 1 \) and \( S_{AA} = 1 \), the interdiffusion coefficient

\[ D = \frac{k_B T}{p_A \xi_4(p_A, 0)} \]  
(4.11)

becomes the same as the center-of-mass diffusion coefficient of a single polymer [15].

A popular approximation step, the Rouse approximation, disregards correlations between solvent forces on different segments in equation (4.7),

\[ \xi_{\alpha\beta}^{mn} = \sum_{s, r = 1}^{N_B} \int_0^\infty \langle f_a^m(t) f_a^n(0) \rangle_{A} \delta_{\alpha\beta} \delta_{mn} \]  

\[ = \xi_4^2(X_A) \delta_{\alpha\beta} \delta_{mn}. \]  
(4.12)

In this approximation the segment friction coefficient becomes independent of polymerization degree, but is still a function of \( X_A \) in general. The Rouse approximation gives a very poor description for dilute polymer solutions. The real justification for discussing this approximation has to be seen in the fact that empirically it is found to give an adequate description of non-entangled polymeric melts.

5. Discussion.

We started our presentation with explaining the discrepancies between two widely used formulas for the interdiffusion coefficient in binary liquids, the Hartley-Crank equation (1.1) and equation (1.2), derived first by de Gennes [1]. Now we have arrived at a third version of an expression for the interdiffusion coefficient, equation (3.27). Since our starting point was quite general, and since we used a minimum of assumptions in order to simplify the equations, this result applies to a wide variety of kinds of binary fluids at arbitrary concentrations. Some examples are : mixtures of simple liquids, isotope mixtures, polymer blends, polymers in a low-molecular weight solvent, colloidal suspensions, a.s.o. In the limit of few A-particles in a background of B-particles, equation (3.27) becomes the self-diffusion or the tracer diffusion coefficient. Especially, if the mass of the A-particles would be much larger than the mass of the B-particles, \( D \) becomes the diffusion coefficient of Brownian motion. For some of these applications we could immediately give the thermodynamic factor \( Q \), as in section 4.1, e.g. In other cases there exist well developed approximation schemes to calculate \( Q \) [16, 17]. The true problem is the evaluation of the coefficients \( A \) or \( \xi(0) \). This affords the solution of a dynamic equation. Even if this task can be performed for special cases, it is always a complicated work. Therefore it would be highly desirable to have an approximate form at hand, which expresses the generalized friction coefficient in terms of a few empirical parameters, corresponding to equation (1.1) or (1.2).

In order to make contact with the Hartley-Crank equation we have to consider the Onsager coefficient \( \Lambda \). If one inserts the definition of \( J_+ \), equation (3.11), in (3.25), \( \Lambda \) can be decomposed [18] as

\[ \Lambda = \frac{1}{N^2_{A} p_{A}^2 \sum_{m=1}^{N_A} \int_0^\infty \sum_{\beta=1}^{P_A} \langle v_m^a(t) v_m^b(0) \rangle_{A}} \]  
+ \[ \frac{1}{N^2_{B} p_{B}^2 \sum_{m=1}^{N_B} \int_0^\infty \sum_{\alpha=1}^{P_B} \langle v_m^a(t) v_m^b(0) \rangle_{B}} \]  
(5.1)

+ terms with velocity correlations between different molecules. The tracer diffusion coefficient (center-of-mass diffusion coefficient) of one polymer of kind \( i \) would be simply given as
If velocity correlations between different polymers can be neglected, equation (5.3) in (3.27) immediately yields the Hartley-Crank equation (1.1). One should note that the \( D_i \) defined by (5.2) still depend on the composition of the system. They have to be understood as the tracer diffusion coefficients of one \( i \)-molecule at the given concentration \( X_i \). So the question about the validity of the Hartley-Crank equation finally reduces to the question whether it is allowed to neglect cross correlations of the velocities of segments of different polymers. In general this cannot be true. For simple liquids computer experiments show the importance of collective vortex motions of the particles [19]. In such a collective vortex motion velocities of different particles will be strongly correlated. But for polymers the chain structure should set a strong limitation to the possibility of such cooperative motions of segments on different polymers and so one might assume that the Hartley-Crank equation (1.1) is a reasonable approximation to the interdiffusion coefficient in polymeric melts sufficiently far away from the glass transition. Close to the glass transition cooperative processes will become important. The argument that velocity cross correlations might be negligible for long polymers becomes especially transparent for entangled polymeric liquids. It is widely accepted that under entanglement constraints the polymers move predominantly in a curvilinear manner (rep-
canonical average as well as the time relaxation of \( f_{1m}^{(i)}(t) \). Most obvious, the number of B-segments, \( N_B p_B \), is lower, for a system with arbitrary composition, compared to the case \( X_A \to 0 \). One might say that the presence of additional A-polymers dilutes the B-system. If we simply assume that this dilution is the most important influence of the additional A-particles, then the probability for an interaction between the A-polymer 1 and a B-polymer 0 is decreased by a factor \( X_B \), compared to the case \( X_A \to 0 \), and

\[
N_B^* \sum_{P_B = 1}^{p_B} \int_0^\infty \left( f_{1m}^{(i)}(t) f_{1}^{(0)}(0) \right) \varphi_T = X_B^2 \xi_{12}^{(1)} . \quad (5.9)
\]

Under this assumption the first term in equation (5.8) can be written

\[
\frac{X_B \xi_1^{(A)}}{(N_A p_A + N_B p_B) p_A} = \frac{k_B T X_B}{(N_A p_A + N_B p_B) p_B D_B} . \quad (5.10)
\]

The second term in (5.9) is the analogous one for one B-polymer in the presence of the A-polymers. By the same reasoning it becomes

\[
\frac{k_B T X_A}{(N_A p_A + N_B p_B) p_B D_B} . \quad (5.11)
\]

Whereas the first two terms in (7.11) depend on the force correlation of one polymer with all polymers of the other kind, the third term depends only on the correlation between an individual pair of polymers, one A-polymer and one B-polymer.

For a dense liquid one might argue that such a correlation should be comparatively short living in time and therefore the contribution of the time integral small, compared to the first two terms. We might therefore neglect this term, which we have done in fact already before, when we assumed equation (5.9). Then we are left with the fourth term in (5.8), which describes a complicated interference of correlation between 4 different polymers, 2 A-polymers and 2 B-polymers. The interdiffusion coefficient (3.27) could now be written as

\[
D = \frac{\frac{X_B^2}{p_A D_A} + \frac{X_A^2}{p_B D_B} + \beta (N_A p_A + N_B p_B) \xi_{44}(0)}{Q} . \quad (5.12)
\]

Up to the interference term this is identical to de Gennes' result (1.2). The structure of this interference term is similar to the hydrodynamic interaction terms discussed in section 4.2. It is hard to see how one could justify to neglect it generally. But for polymeric mixtures we might again use our empirical knowledge, that their dynamic is well described by a Rouse-model, which neglects hydrodynamic interactions. Microscopically, this observation can only be understood if interference terms, like in the fourth term in equation (5.8), are negligible. Then equation (5.12) would agree with the RPA result (1.2).

To make our point clear, we do not really want to say that either equation (1.1) or (1.2) are the correct expressions for the interdiffusion coefficient. Rather we wanted to show here the arguments by which these simplified formulas could be derived from the rigorous microscopic result (3.27). From these discussions one gets now the impression that for polymeric melts reasonable arguments can be given in support of both formulas, equations (1.1) and (1.2)! This poses the question whether both expressions could be valid as a reasonable approximation. This can be true only when

\[
p_A D_A = p_B D_B . \quad (5.13)
\]

For mixtures of homopolymers with different polymerization degree this condition is indeed obeyed by the Rouse model, equation (4.12), which is generally accepted as a good description of nonentangled melts. For high molecular weight entangled melts it is widely believed that dynamic processes are dominated by a curvilinear motion (reptation) of the molecules. The standard model [20] yields

\[
D_i = \frac{1}{3} \frac{k_B T}{p_i} \xi_0^{(i)} p_i , \quad (5.14)
\]

which would be in strong disagreement with condition (5.13) and gives very different results when inserted in equations (1.1) or (1.2), respectively. \( p_c \) is a critical polymerization degree at which entanglements become effective. But another microscopic and selfconsistent treatment of the motion of polymers under entanglement conditions, which was recently published by one of us, shows much stronger influence of matrix effects on the motion of a tracer polymer [21]. Instead of equation (5.14) one obtains

\[
D_i = \frac{1}{4} \frac{k_B T}{p_i} \left[ p_c + p_c \right] , \quad i = A \text{ or } B , \quad (5.15)
\]

for homopolymers (\( \xi_0^{(A)} = \xi_0^{(B)} \)). This formula is again in agreement with condition (5.13). From both formulas (1.1) and (1.2) one would then obtain an interdiffusion coefficient

\[
D = \frac{1}{4} \frac{k_B T}{\xi_0} \left[ p_c + p_c \right] Q . \quad (5.16)
\]

This result is similar to the one, which is obtained when the reptation model (5.14) is inserted in the Hartley-Crank equation (1.1). Both results tell that the interdiffusion process is dominated by the motion of the smaller molecules. This is indeed what was found in recent experiments [22, 23], but the under-
lying reasons for this correspondence are quite
different.
If we want to consider mixtures of chemically
different polymers, the discussion becomes very
difficult. It is important to stress that the segment
friction coefficients occurring in equations (4.12,
5.14 or 5.15), are not elementary intrinsic properties
of the molecules. They themselves depend on the
composition of the mixture, on the configurational
relaxation times of both kinds of molecules in a
complicated and so far unknown manner. It was
mentioned before that close to the glass temperature
of one of the species the arguments leading to the
Hartley-Crank equation become questionable, be-
cause of the cooperative nature of the transition.
This can be shown by a simple example. Let us
assume that species A is already in a glassy state, but
the molecules of species B are not. This corresponds
to the picture of polymers B moving in a glassy
matrix, made up of A-molecules. Of course there
can be no interdiffusion in this situation. Therefore
$D = 0$, $D_A = 0$ and $D_B \neq 0$. These conditions are
compatible only with the RPA-result (1.2), but not
with the Hartley-Crank equation (1.1). Recent ex-
periments [24] also showed that interdiffusion is
dominated by the species which is closer to the glass
transition, in agreement with equation (1.2).

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References

1312.
[8] MURSCHALL, U., FISCHER, E. W. and HERKT-
[12] ZWANZIG, R., Lectures in Theoretical Physics, Ed.
57 (1972) 2098.
[15] YAMAKAWA, H., Modern Theory of Polymer Sol-
[16] See, e.g.: MARCH, N. H. and TOSI, M. P., Atomic
Dynamics in Liquids (MacMillan, London)
1977.
[17] AKCASU, A. Z., BENMOUNA, M. and BENOIT, H.,
[18] JACUCCI, G. and MACDONALD, I. R., Physica 80A
(1975) 607.
Physics (Cornell University, Ithaka) 1979.
[22] COMPOSTO, R. J., KRAMER, E. J. and WHITE, D. M.
(to be published).
[24] MURSCHALL, U., FISCHER, E. W., HERKT-MAETZ-
Lett. 24 (1986) 191 ;
BRERETON, M. G., FISCHER, E. W., FYTAS, G. and
5174.