Gaussian chains where the finiteness of the generalized moment $\langle |\mathbf{R}|^{\alpha} \rangle$ requires $\alpha < 1/\nu_L$ (see: Prentis, J. J. *J. Phys. A* **1985**, *18*, L833). Prentis considers the excluded volume perturbation expansion based on the interaction (2.3a) which generalizes the TP perturbation expansion, and he renormalizes the theory to obtain the exponent ν_L with excluded volume. We can also add the surface interaction (2.2c) and can no doubt obtain the infinite-order expansion through a slight generalization of the calculation of section III. The surface interaction crossover exponent in this case is $\phi_s' = \epsilon'\nu_L$, $\epsilon' = 1/\nu_L - d_\perp$, which reduces to the exponent given in (2.2d) for $\nu_L = {}^1/_2$. The probability of return to a hypersurface of dimension $d_\parallel = d - d_\perp$ should be less than unity for $d_\perp > 1/\nu_L$. Hughes (see above) has proven this for the special case of $d_\parallel = 0$, corresponding to a return to a point. Also the general arguments in Appendix A lead to the expectation of a fractional-order adsorption phase transition of order $1/\phi_s'$ for a Lévy flight chain onto a hypersurface of integer dimension.

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Mutual Diffusion in Concentrated Polymer Solutions under a Small Driving Force

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ABSTRACT: A theory is presented for mutual diffusion in concentrated polymer solutions under a small driving force. The crucial concept is that the interdiffusion of polymer and solvent causes deformation of the polymer component. A memory integral contribution to the solvent flux is developed from the transient network and reptation models; analytical formulas for measurables are derived for a polymer behaving like a Maxwell fluid. For sorption experiments, non-Fickian behavior is predicted when the polymer relaxation time matches the sorption time scale, that is, when the diffusion Deborah number is $\sim\mathcal{O}(1)$. The predictions agree with non-Fickian behavior observed in classical and oscillatory sorption experiments. The analysis clarifies the potential value of the oscillatory sorption technique.

I. Introduction

The diffusion of a low molecular weight species in high polymer systems over a macroscopic length scale is often the rate-controlling process in industrial processing operations; examples include fiber spinning, film casting, and coatings processes. The effective design of these requires a quantitative description of the diffusion. Our recent work[1,2] focuses on mutual diffusion in concentrated polymer solutions under a small driving force, that is, the interdiffusion of solvent and polymer in the presence of a slight composition gradient. A theory based on the physical arguments of Thomas and Windle[3] compares reasonably well with data over a range of conditions encompassing the so-called viscoelastic[4,5] or non-Fickian regime. In this article we present an alternate development of the theory and analyze sorption under a small driving force.

II. Sorption Experiments

In the classical sorption experiment, a polymer solution is held in contact with a large reservoir of solvent vapor at temperature T and pressure P. The solvent activity in the vapor, $a(t)$, is increased in a step

$$a(t) = a^- + AH(t) \qquad \text{(II.1)}$$

causing diffusion of solvent into the solution. Here, a^- is the activity before the step ($0 < a^- < 1$), $H(t)$ is the step function, and A is the amplitude of the step ($a^- + A < 1$). Commonly, one observes the total mass of solvent in the solution, $M(t)$. In a more general experiment

$$a(t) = a^- + Ag(t) \qquad \text{(II.2)}$$

where $g(t)$ is a bounded, piecewise continuous function. (If $-1 < g(t) < 1$, then A lies in a range such that $0 < a^- - A$ and $a^- + A < 1$.)

Very little experimental work has been done with $g(t) \neq H(t)$. Vrentas, Duda, and co-workers[6] reported recently on a technique using $g(t) = \sin \omega t$. The method, called oscillatory sorption, appears promising for the study of mutual diffusion in polymer solutions and is analyzed subsequently in some detail.

For simplicity we consider sorption in one-dimensional systems (Figure 1) having an average depth l and allow only small fluctuations in $a(t)$; i.e., $A \ll 1$. Before we continue, a summary of previous work is given.

III. Previous Theory

Mutual diffusion on a macroscopic length scale (say >10 μm) is described adequately by the species continuity equations together with constitutive relationships for the

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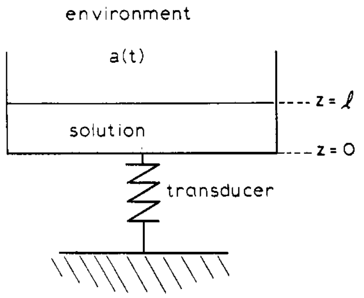

Figure 1. Schematic representation of a one-dimensional sorption experiment.

species flux and appropriate initial and boundary conditions. Under a small driving force, variations in composition are small and composition-dependent properties can be treated as constants.

Continuity for species i is

$$\frac{\partial}{\partial t}\rho_i = -\frac{\partial}{\partial \mathbf{r}}\cdot\mathbf{j}_i = -\frac{\partial}{\partial \mathbf{r}}\cdot\rho_i\mathbf{v}^{(i)} \qquad \text{(III.1)}$$

where ρ_i is the mass density of i (1, solvent; 2, polymer), $\mathbf{r}$ is the position in the lab frame, $\mathbf{j}_i$ is the mass flux of i in the lab frame, and $\mathbf{v}^{(i)}$ is the local average velocity of i in the lab frame.

For one-dimensional mutual diffusion, it proves convenient to transform (III.1) to the polymer fixed coordinates,[7] employing the dilating length scale $\xi = \int_{z*}^{z}\rho_2\hat{V}_2\,\mathrm{d}z'$, with $\hat{V}_2$ being the partial specific volume of 2 and $z*$ being a reference position where the polymer flux vanishes (e.g., $z* = 0$ in Figure 1). When the volume change on mixing is neglected, III.1 gives

$$\frac{\partial}{\partial t}C = -\frac{\partial}{\partial \xi}j_1^{\,2} \qquad \text{(III.1a)}$$

for $i = 1$ and a trivial identity for $i = 2$. Here, $C = \rho_1/\rho_2\hat{V}_2$ and $j_1^{\,2} = \rho_1(v^{(1)} - v^{(2)})$ means the mass flux of the solvent relative to the polymer.

Specifying the flux is the key in constructing an adequate theory for mutual diffusion. The classical theory results from Fick's law

$$\mathbf{j}_1^{\,2} = -\frac{D_{12}}{\rho_2\hat{V}_2}\frac{\partial}{\partial \mathbf{r}}\rho_1 \qquad \text{(III.2)}$$

or

$$j_1^{\,2} = -D_{12}(\rho_2\hat{V}_2)^2\frac{\partial C}{\partial \xi} = -D\frac{\partial C}{\partial \xi} \qquad \text{(III.2a)}$$

for a one-dimensional process. Here D_{12} means the binary mutual diffusion coefficient.

Fick's law can be derived for condensed mixtures from nonequilibrium thermodynamics[8a,b] or kinetic theory;[9] our discussions focus on the former approach. Two distinct developments of the thermodynamics exist: the linear irreversible theory accepting the Gibbs equation locally[8a] and the rational thermodynamics[8b] exploring the mathematical consequences of a collection of axioms on entropy and material behavior. Both require that the local entropy production, σ, be nonnegative identically

$$\sigma \geq 0 \qquad \text{(III.3)}$$

The linear, irreversible theory leads to

$$\mathbf{j}_1^{\,2} = -\frac{\Omega\rho}{\omega_2 M_1\rho_2}\left(\frac{\partial}{\partial \mathbf{r}}\mu_1\right)_{T,P} \qquad \text{(III.4)}$$

as the simplest expression ensuring the inequality III.3 in an isothermal system. Here, μ_1 is the local molar chemical potential of 1, M_1 is the molecular weight of 1, Ω is a positive, phenomenological coefficient depending on composition, and ω_i is the mass fraction of i. The chemical potential has the definition

$$\frac{1}{M_1}(\mu_1 - \mu_1{}^{\circ}) = (\rho_2\hat{V}_2)^2\left(\frac{\partial}{\partial \rho_1}(\check{\Phi}/\rho_2\hat{V}_2)\right) = \left(\frac{\partial}{\partial \rho_1}\check{\Gamma}\right)_{\rho_2,T} = \rho\left(\frac{\partial}{\partial \rho_1}\hat{\Gamma}\right)_{\rho_2,T} \qquad \text{(III.5)}$$

where $\mu_1{}^{\circ}$ means the standard potential, Φ means the change in the Gibbs function on mixing, Γ means the change in Helmholtz function on mixing, and $\rho = \rho_1 + \rho_2$ means the mass density of the mixture. The linear irreversible theory presumes that Γ is a unique function of temperature, pressure, and composition so that

$$\frac{\mu_1 - \mu_1{}^{\circ}}{RT} = \ln a' = f(\rho_1,T,P) \qquad \text{(III.6)}$$

where a' is the solvent activity in the solution and R is the gas constant. Consequently, one gets (III.2) for the flux with

$$D_{12} = \frac{\Omega RT}{M_1\rho_2}\left(\frac{\partial f}{\partial \omega_1}\right)_{T,P} \qquad \text{(III.7)}$$

for the mutual diffusion coefficient.

Equations III.1 and III.2 can describe mutual diffusion in polymer solutions over a limited range of conditions; Vrentas, Duda, and co-workers[4,5] clarified the range of validity for diffusion under a small driving force with the diffusion Deborah number λ/t_{D}. Here λ is an average rheological relaxation time for the solution and t_{D} the characteristic time for diffusion according to the classical theory. Evidently, the classical theory works well when $\lambda/t_{\mathrm{D}} \ll 1$ but fails when $\lambda/t_{\mathrm{D}} \sim \mathcal{O}(1)$, where the unusual "viscoelastic" or "non-Fickian" diffusion appears. For mutual diffusion over a macroscopic length scale viscoelastic behavior usually occurs in concentrated solutions and within ~20 °C of the glass transition temperature for the mixture.

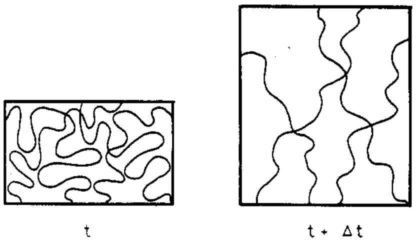

Figure 2. Schematic representation of the polymer component in a small volume element during one-dimensional mutual diffusion; the accumulation of solvent causes a deformation of the polymer structure.

Thomas and Windle[3] developed a modified flux relationship from plausible physical arguments to account for viscoelastic diffusion. They postulated that the local accumulation of solvent entails a deformation of the physcial network of entangled chains as depicted in Figure 2. Since the network resists deformation the solvent experiences a flow-dependent traction with an isotropic component Π. The authors suggested that Π affects the solvent chemical potential like a hydrostatic pressure

$$\frac{\mu_1 - \mu_1{}^{\circ}}{RT} = f(\rho_1,T,P) + \frac{1}{RT}\int_{P}^{P+\Pi}\frac{\partial \mu_1}{\partial P'}\,\mathrm{d}P' \qquad \text{(III.8)}$$

On an empirical basis Thomas and Windle postulated

$$\Pi_\xi = \eta_l \hat{V}_1 (\partial C/\partial t)_\xi \tag{III.9}$$

for one-dimensional diffusion, where η_l is the longitudinal viscosity of the polymer phase and $\hat{V}_1(\partial C/\partial t)_\xi$ represents its effective local strain rate. Equation III.9 implies purely viscous rheological behavior of the polymer component and leads to the flux

$$j_1^{\,2} = -D\frac{\partial C}{\partial \xi} - D'\frac{\partial^2 C}{\partial \xi\,\partial t} \tag{III.10}$$

with

$$D' = \frac{D\bar{V}_1}{RT}\,\frac{\rho\hat{V}_1}{\rho_2\hat{V}_2\omega_2}\left(\frac{\partial f}{\partial \omega_1}\right)^{-1}\eta_l \tag{III.10a}$$

for a one-dimensional process under a small driving force. Durning, Spencer, and Tabor[1] studied the predictions of (III.1a) and (III.10) and found a non-Fickian behavior; however, the predictions do not agree with observations in the non-Fickian regime.

Durning[2] revised (III.9) by assuming

$$\eta_l\hat{V}_1\left(\frac{\partial C}{\partial t}\right)_\xi = \tau_l\left(\frac{\partial \Pi}{\partial t}\right)_\xi + \Pi_\xi \tag{III.11}$$

which implies simple viscoelastic behavior of the polymer phase. Here τ_l means the longitudinal relaxation time of the polymer component. Equations III.4, III.7, III.8, and III.11 lead to

$$j_1^{\,2} = -D\frac{\partial C}{\partial \xi} - D'\frac{\partial}{\partial \xi}\int_{-\infty}^{t} e^{-(t-t')/\tau_l}\left(\frac{\partial C}{\partial t'}\right)\mathrm{d}t' \tag{III.12}$$

with

$$D' = \frac{D\bar{V}_1}{RT}\,\frac{1}{\omega_2^{\,2}}\left(\frac{\partial f}{\partial \omega_1}\right)^{-1}\left(\frac{\hat{V}_1}{\hat{V}_2}\right)\frac{\eta_l}{\tau_l} \tag{III.12a}$$

Combination of (III.1a) and (III.12) gives a satisfying analytical description of mutual diffusion under a small driving force. The theory predicts non-Fickian behavior when $\tau_l D/l^2 \sim \mathcal{O}(1)$, in reasonable accord with that observed in sorption experiments.

In recent, parallel developments, Brochard and de Gennes[10a] and Jäckle and Frisch[10b,c] discuss flux relationships resembling (III.12). Both developments adopt eq III.4 and take μ_1 (or, equivalently, the osmotic pressure) to have a fading memory of the local concentration history. Brochard and de Gennes[10a] examine mutual diffusion in semidilute solutions with a good solvent and attribute the fading memory in μ_1 to slow chain disentanglement during diffusion, an idea resembling Thomas and Windle's in constructing (III.8) and (III.9). Jäckle and Frisch[10b,c] examine mutual diffusion in a glassy system and attribute the fading memory in μ_1 to slow structural changes affecting short-ranged interactions between the polymer segments and solvents.

In summary, the recent studies encourage the view that a relation of the form (III.12) captures the essential features of mutual diffusion in concentrated polymer systems.

IV. Alternate Derivation of the Flux

1. Thermodynamics. The specific free energy of a polymeric liquid, $\hat{\Gamma}$, depends on the state and history of the deformation of the polymer component (see, for example, Lodge[11a]). This implies an influence of the polymer rheological properties on mutual diffusion since the polymer is deformed during the process and $\hat{\Gamma}$ determines the driving force. To describe this influence precisely we suppose that $\hat{\Gamma}$ depends objectively on the displacement gradient of the polymer, $\mathbf{E}^{(2)}$ and on its history, $\mathbf{E}^{(2)}(s)$. Also, we specify the entropy flux in the system as

$$\eta = \frac{\mathbf{q}}{T} - \frac{1}{T}\left[\rho\left(\frac{\partial}{\partial \rho_1}\hat{\Gamma}\right)_{\rho_2,T,\{\alpha\}}\mathbf{J}_1 - \rho\left(\frac{\partial}{\partial \rho_2}\hat{\Gamma}\right)_{\rho_1,T,\{\alpha\}}\mathbf{J}_2\right] \tag{IV.1}$$

where $\mathbf{q}$ is the heat flux, $\mathbf{J}_i = \rho_i(\mathbf{v}_i - \mathbf{v})$ is the mass flux of i relative to the barycentric velocity $\mathbf{v}$, and $\{\alpha\}$ means the set of independent variables influencing $\hat{\Gamma}$ other than composition and temperature.

These assumptions lead to a simple relation for the flux (Appendix A)

$$\mathbf{J}_1 = \omega_2\mathbf{j}_1^{\,2} = -\Omega\frac{\partial}{\partial \mathbf{r}}\Delta \tag{IV.2}$$

where Ω is a positive phenomenological coefficient and Δ means $\rho[((\partial/\partial\rho_1)\hat{\Gamma})_{\rho_2,T,\{\alpha\}} - ((\partial/\partial\rho_2)\hat{\Gamma})_{\rho_1,T,\{\alpha\}}]$. For mutual diffusion under a small driving force, the relation

$$\frac{\partial}{\partial \mathbf{r}}\rho\left(\frac{\partial}{\partial \rho_1}\hat{\Gamma}\right)_{\rho_2,T,\{\alpha\}} = -\frac{\omega_2}{\omega_1}\,\frac{\partial}{\partial \mathbf{r}}\rho\left(\frac{\partial}{\partial \rho_2}\hat{\Gamma}\right)_{\rho_1,T,\{\alpha\}} \tag{IV.3}$$

holds to within an arbitrarily small error provided the thermodynamic pressure, $P = \rho[\rho_1((\partial/\partial\rho_1)\hat{\Gamma})_{\rho_2,T,\{\alpha\}} + \rho_2((\partial/\partial\rho_2)\hat{\Gamma})_{\rho_1,T,\{\alpha\}}]$, remains constant during the process (Appendix B). Under these conditions, eq IV.2 can be put in the form of eq III.4 with

$$\frac{1}{M_1}(\mu_1 - \mu_1^{\circ}) = (\rho_2\hat{V}_2)^2\left(\frac{\partial}{\partial \rho_1}(\check{\Phi}/\rho_2\hat{V}_2)\right)_{\rho_1,T,\{\alpha\}} \tag{IV.4}$$

and with Ω being a positive constant to within an arbitrarily small error.

2. Kinetic Theory. We now develop expressions for μ_1 in deforming polymer solutions from two well-accepted models of concentrated systems: the transient network model,[11a,b] and the reptation model.[12a–e] In both developments we assume small deformations of the polymer component, locally homogeneous deformation of the polymer, and a small divergence of $\mathbf{v}^{(2)}$.

Consider a polymer material volume in a deforming solution large enough to contain a statistical number of chains but small enough so that the deformation is homogeneous and the composition is uniform. We assume the free energy density in the element relative to the pure, undeformed components can be written

$$\check{\Phi} = \check{\Phi}^{\mathrm{m}} + \check{\Phi}^{\mathrm{f}} \tag{IV.5}$$

where $\check{\Phi}^{\mathrm{m}}$ is the free energy density change on mixing the pure, undeformed components and $\check{\Phi}^{\mathrm{f}}$ is the flow-dependent part of $\check{\Phi}$.

2a. Transient Network Model. According to the transient network model

$$\check{\Phi}^{\mathrm{f}} = \sum_{n,i}\langle\phi_i(|\mathbf{R}|)\rangle_{in} \tag{IV.6}$$

where ϕ_i means the free energy relative to the undeformed state of a strand in the network having i structural units and an end to end distance $|\mathbf{R}|$. Here, $\langle x\rangle_{in}$ means the expectation value of x

$$\langle x\rangle_{in} = \int f_{in}(|\mathbf{R}|,t)x\,\mathrm{d}^3\mathbf{R} \tag{IV.7}$$

where f_{in} is the number distribution of strands with i structural units and having junctions of type n; $\mathrm{d}^3\mathbf{R}$ is the volume element for the distribution function.

For chainlike strands experiencing small deformations[13]

$$\phi_i(|R|) = -kT\ln\frac{Q_i(|\mathbf{R}|)}{Q_i(|\mathbf{R}|=0)} = \frac{1}{2}H_i|\mathbf{R}|^2 \tag{IV.8}$$

with

$$H_i = kT\frac{1}{\bar{R}_0^2}\left[1 - \frac{\partial \ln \bar{R}_0^2}{\partial \ln T}\right] \qquad \text{(IV.8a)}$$

Here, k is Boltzman's constant, Q_i is the canonical partition function for the strand, and $\bar{R}_0^2$ is the equilibrium mean square end-to-end length of the undeformed strand. Note that eq IV.8 applies for any chainlike strand provided the extension is small and $R_0 = 0$.

One needs to evaluate $\langle|\mathbf{R}|^2\rangle_{in}$; a convenient procedure is to evaluate $\langle\mathbf{RR}\rangle_{in}$ and form the trace (Tr) of the result. We assume that the strand distribution function obeys the conversation equation

$$\frac{\partial f_{\text{in}}}{\partial t} = -\frac{\partial}{\partial \mathbf{R}}\cdot\left(f_{\text{in}}\mathbf{R}\cdot\frac{\partial}{\partial \mathbf{r}}\mathbf{v}^{(2)}\right) + L_{in}(\rho_2,|\mathbf{R}|,t) - \frac{f_{\text{in}}}{\tau_{\text{in}}(\rho_2,t)} \qquad \text{(IV.9)}$$

which says the network junctions move affinely with the polymer phase. Here, $L_{in}(\rho_2,|\mathbf{R}|,t)$ means the rate of creation of network junctions of type n defining strands having i structural units and $\tau_{\text{in}}(\rho_2,t)$ means the corresponding strand lifetime. Taking moments of (IV.9) leads to a dynamic relationship for $\langle\mathbf{RR}\rangle_{in}$ that can be integrated in convected coordinates.[11b] The result leads to

$$\breve{\Phi}^{\text{f}} = \frac{1}{2}\int_{-\infty}^{t} M_{\text{T}}(\rho_2,t,t')[3 - \text{Tr}\ \gamma^{(2)}(\mathbf{r},t,t')]\ \text{d}t' \qquad \text{(IV.10)}$$

in the limit of small deformations. Here

$$M_{\text{T}}(\rho_2,t,t') = \sum_{i,n} H_{in}\bar{L}_{in}(\rho_2,t')\exp\left[-\int_{t'}^{t}\frac{\text{d}t''}{\tau_{in}(\rho_2,t'')}\right] \qquad \text{(IV.11)}$$

with

$$\bar{L}_{in}(\rho_2,t) = \frac{4}{3}\pi\int_0^\infty r^4 L_{in}(\rho_2,r,t)\ \text{d}r \qquad \text{(IV.12)}$$

is the memory function for the network. Also, $\gamma^{(2)}(\mathbf{r},t,t')$ is the infinitesimal strain tensor for the polymer phase; the argument $\mathbf{r}$ in $\gamma^{(2)}$ indicates the location of the volume element.

To simplify calculation of μ_1 we specialize (IV.11) to include only one type of junction (i.e., a single value of n) and take $L_{in} = L_i(\rho_2)$ and $\tau_{in} = \tau_i(\rho_2)$ to be constants. Then (IV.10) can be integrated by parts to give

$$\breve{\Phi}^{\text{f}} = G_{0,\text{T}}\int_{-\infty}^{t}\phi_T(\rho_2,t-t')\ \text{Tr}\ \frac{1}{2}\dot{\gamma}^{(2)}(\mathbf{r},t')\ \text{d}t' \qquad \text{(IV.13)}$$

where

$$\phi_T(\rho_2,t-t') = \frac{1}{G_{0,\text{T}}}\sum_i H_i L_i(\rho_2)\tau_i(\rho_2)e^{-(t-t')/\tau_i(\rho_2)} \qquad \text{(IV.13a)}$$

is the (dimensionless) relaxation function for the network and

$$G_{0,\text{T}}(\rho_2) = \sum_k H_k L_k(\rho_2)\tau_k(\rho_2) \qquad \text{(IV.13b)}$$

is the instantaneous modulus of the network. The tensor $\dot{\gamma}^{(2)}$ is the infinitesimal rate of strain tensor for the polymer phase. Equations IV.4 and IV.13 allow straightforward calculation of μ_1 since the integral in (IV.13) can be treated as constant during the differentiation; the result is

$$\mu_1 - \mu_1^\circ = RTf(\rho_2,T,P) + \bar{V}_1 G_{0,\text{T}}\int_{-\infty}^{t}\phi_T(\rho_2,t-t')\ \text{Tr}\ \frac{1}{2}\dot{\gamma}^{(2)}(\mathbf{r},t')\ \text{d}t \qquad \text{(IV.14)}$$

2b. Reptation Model. We adopt the independent alignment approximation in the reptation model, consequently[12b,c,14a,b]

$$\Phi^{\text{f}} = n_2 NRT\left\langle \ln\frac{f(\mathbf{u},s,t)}{f(\mathbf{u}_0,s,t)}\right\rangle \qquad \text{(IV.15)}$$

where n_2 is the molar concentration of polymer chains, N is the number of primitive segments per chain, and $f(\mathbf{u},s,t)$ is the orientation distribution function in the deformed state for a primitive segment located a distance s along the primitive chain; $f(\mathbf{u}_0,s,t)$ is the corresponding distribution function in the undeformed fluid. Here, $\mathbf{u}$ is a unit vector tangent to the primitive chain at s. Also, $\langle x\rangle$ means the average value of x

$$\langle x\rangle = \frac{1}{L}\int_0^L\int f(\mathbf{u},s,t)x\ \text{d}s\ \text{d}^2\mathbf{u} \qquad \text{(IV.16)}$$

where L is the contour length of the primitive chain and $\text{d}^2\mathbf{u}$ is a volume element in orientation space.

In the limit of small deformations of the polymer phase, the independent alignment approximation allows[14a,b]

$$\ln\frac{f(\mathbf{u},s,t)}{f(\mathbf{u}_0,s,t)} \simeq 3 - \text{Tr}\ \gamma'^{(2)} - 3\mathbf{u}\cdot(\delta - \dot{\gamma}'^{(2)})\cdot\mathbf{u} \qquad \text{(IV.17)}$$

where δ is the unit tensor and $\dot{\gamma}'^{(2)}$ the infinitesimal displacement gradient in the polymer phase.

To compute the average of (IV.17), the distribution function is needed; we assume $f(\mathbf{u},s,t)$ obeys

$$\frac{\partial}{\partial t}f(\mathbf{u},s,t) = \mathcal{D}\frac{\partial^2}{\partial s^2}f(\mathbf{u},s,t) - \frac{\partial}{\partial \mathbf{u}}\cdot\mathbf{G}(\mathbf{u})f(\mathbf{u},s,t) \qquad \text{(IV.18)}$$

with

$$\mathbf{G}(\mathbf{u}) = \frac{\partial}{\partial \mathbf{r}}\mathbf{v}^{(2)}\cdot\mathbf{u} - \left[\mathbf{u}\cdot\frac{\partial}{\partial \mathbf{r}}\mathbf{v}^{(2)}\cdot\mathbf{u}\right]\mathbf{u} \qquad \text{(IV.18a)}$$

which says the primitive segments move affinely with the polymer phase. Here, $\mathcal{D}$ is the curvilinear diffusion coefficient characterizing Brownian motion along the primitive chain contour ($\mathcal{D} = 3ND_2$, where D_2 is the polymer self-diffusion coefficient). Doi and Edwards[12c] solved (IV.18) for homogeneous flows; their result leads to

$$\breve{\Phi}^{\text{f}} = \frac{n_2 NRT}{4\pi}\int_{-\infty}^{t}\int M_{\text{R}}(\rho_2,t-t')[\mathbf{T}(\mathbf{u}) - \text{Tr}\ \gamma'^{(2)}(\mathbf{r},t,t')]\ \text{d}t'\ \text{d}^2\mathbf{u} \qquad \text{(IV.19)}$$

with

$$\mathbf{T}(\mathbf{u}) = \frac{3(\gamma'^{(2)}\cdot\mathbf{u})\cdot\gamma'^{(2)}\cdot(\gamma'^{(2)}\cdot\mathbf{u})}{|\gamma'^{(2)}\cdot\mathbf{u}|^2} \qquad \text{(IV.19a)}$$

Here

$$M_{\text{R}}(\rho_2,t-t') = n_2 NRT\sum_{p\ \text{odd}}\frac{8}{p^2\pi^2\tau_p(\rho_2)}e^{-(t-t')/\tau_p(\rho_2)} \qquad \text{(IV.20)}$$

is the memory function according to the reptation model; the $\tau_p(\rho_2) = L^2/\mathcal{D}\pi^2p^2$ are the corresponding relaxation times. In the limit of small deformations $\mathbf{T} \cong \delta$ and (IV.19) can be integrated by parts to give an expression analogous to (IV.14) for μ_1 but with the relaxation function

$$\phi_{\text{R}}(\rho_2,t-t') = \frac{1}{G_{0,\text{R}}}\sum_{p\ \text{odd}}\frac{8}{p^2\pi^2}e^{-(t-t')/\tau_p(\rho_2)} \qquad \text{(IV.21)}$$

replacing ϕ_T, the instantaneous modulus

$$G_{0,\mathrm{R}} = n_2NRT \sum_{q\,\mathrm{odd}} \frac{8}{q^2\pi^2} \qquad \text{(IV.21a)}$$

replacing $G_{0,T}$, and the rate of strain tensor $\dot{\gamma}'^{(2)}$ replacing $^1/_2\dot{\gamma}^{(2)}$.

We can now establish the form of the flux for mutual diffusion under a small driving force by combining the results for μ_1 with eq III.4 and IV.4. Note that in a one-dimensional process $\mathbf{v}^{(2)} = (0, 0, v_z{}^{(2)}(z))$, so

$$\mathrm{Tr}\ {}^1\!/_2\dot{\gamma}^{(2)} = \mathrm{Tr}\ \dot{\gamma}'^{(2)} = \frac{\partial v_z{}^{(2)}}{\partial z} \qquad \text{(IV.22)}$$

The integration of (III.1) for $i = 2$ gives

$$\frac{\partial v_z{}^{(2)}}{\partial z} = -\frac{\partial}{\partial z}\frac{1}{\rho_2}\int_{z*}^{z}\left(\frac{\partial \rho_2}{\partial t}\right)\mathrm{d}z' \qquad \text{(IV.23)}$$

and transformation to the polymer fixed frame under the assumption of constant partial specific volumes (Appendix C) provides

$$\frac{\partial v_z{}^{(2)}}{\partial z} = \hat{V}_1(\rho_2\hat{V}_2)\left(\frac{\partial C}{\partial t}\right)_{\xi} \qquad \text{(IV.24)}$$

Collecting (III.4), (IV.4), (IV.14), (IV.22), and (IV.24) leads to a one-dimensional flux of the form

$$j_1{}^2 = -D\frac{\partial C}{\partial \xi} - D'\frac{\partial}{\partial \xi}\int_{-\infty}^{t}\phi(t-t')\left(\frac{\partial C}{\partial t'}\right)\mathrm{d}t' \qquad \text{(IV.25)}$$

with

$$D' = \frac{D\bar{V}_1}{RT}\frac{1}{\omega_2}\left(\frac{\partial f}{\partial \omega_1}\right)^{-1}\rho\hat{V}_1G_0 \qquad \text{(IV.26)}$$

Here, ϕ and G_0 are generic representations of the relaxation function and instantaneous modulus of the polymer phase evaluated at the mean composition of the mixture.

The flux (IV.25) is essentially the same as that postulated earlier on an empirical basis (eq III.12).

V. Equations Governing Sorption

A linear integrodifferential equation[15] representing an unsteady solvent mass balance results from the combination of (III.1a) and (IV.25)

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial \xi^2} + D'\frac{\partial^2}{\partial \xi^2}\int_{-\infty}^{t}\phi(t-t')\left(\frac{\partial C}{\partial t'}\right)\mathrm{d}t' \qquad \text{(V.1)}$$

To get analytical results for measurable quantities, we include the case of the polymer phase behaving like a Maxwell fluid. Then

$$\phi(t-t') = e^{-(t-t')/\tau} \qquad \text{(V.2a)}$$

and

$$G_0 = \frac{\eta}{\tau} \qquad \text{(V.2b)}$$

with η being a viscosity and τ being the corresponding relaxation time, both evaluated at the mean composition during the diffusion. For the Maxwell model, eq V.1 can be rearranged to

$$\frac{\partial^2 C}{\partial t^2} + \frac{1}{\tau}\frac{\partial C}{\partial t} = \frac{D}{\tau}\frac{\partial^2 C}{\partial \xi^2} + (D + D')\frac{\partial^3 C}{\partial \xi^2\,\partial t} \qquad \text{(V.3)}$$

with G_0 in D' given by (V.2b). The last expression is that developed in previous work[2] based on (III.12).

Two boundary conditions must be specified to develop solutions for $C(\xi,t)$ and $M(t)$ during sorption. For the one-dimensional system in Figure 1, the solvent flux vanishes at $z = 0$, giving

$$0 = D\frac{\partial C}{\partial \xi} + D'\frac{\partial}{\partial \xi}\int_{-\infty}^{t}\phi(t-t')\left(\frac{\partial C}{\partial t'}\right)\mathrm{d}t' \qquad \text{(V.4)}$$

or

$$0 = \frac{D}{\tau}\frac{\partial C}{\partial \xi} + (D + D')\frac{\partial^2 C}{\partial \xi\,\partial t} \qquad \text{(V.5)}$$

for the Maxwell fluid provided G_0 in D' is given by (V.2b).

For the boundary condition at the interface between the solution and the environment we assume continuity of the potential, μ_1, or

$$a(t) = a'(\xi{=}l) \qquad \text{(V.6)}$$

The results for μ_1 developed in section IV lead to

$$\ln a(t) = f|_{\xi=l} + G\int_{-\infty}^{t}\phi(t-t')\left(\frac{\partial C}{\partial t'}\right)_{\xi=1}\mathrm{d}t' \qquad \text{(V.7)}$$

where

$$G = \frac{\bar{V}_1G_0\hat{V}_1\rho_2\hat{V}_2}{RT} \qquad \text{(V.7a)}$$

For concentrated solutions, the Flory–Huggins theory gives an accurate formula for f; for mathematical convenience we adopt an approximate version

$$f = \ln C/K \qquad \text{(V.8a)}$$

with

$$\ln K = -\ln \hat{V}_1 - (1 + \chi) \qquad \text{(V.8b)}$$

where χ means the Flory–Huggins parameter.

With (V.8) and the approximation that the second term on the right in (V.7) is small, the boundary condition at $\xi = l$ can be written

$$C(\xi{=}l,t) = a(t)K\left[1 - G\int_{-\infty}^{t}\phi(t-t')\left(\frac{\partial C}{\partial t'}\right)_{\xi=1}\mathrm{d}t'\right] \qquad \text{(V.9)}$$

For the Maxwell fluid the result is

$$[1 + a(t)KG]\frac{\partial C}{\partial t} + \left[\frac{1}{\tau} - \frac{\mathrm{d}\ln a(t)}{\mathrm{d}t}\right]C = \frac{a(t)K}{\tau} \qquad \text{(V.10)}$$

Scaling simplifies the notation; the variables

$$u = \frac{C(\xi,t) - Ka^-}{KA} \qquad s = \frac{Dt}{l^2} \qquad x = \frac{l - \xi}{l} \qquad \text{(V.11)}$$

lead to dimensionless versions of (V.1), (V.4), and (V.9)

$$u_s = u_{xx} + k_0\int_{-\infty}^{s}\phi(s-s')u_{xxs'}\,\mathrm{d}s' \qquad \text{(V.12)}$$

$$u_x|_{x=1} + k_0\int_{-\infty}^{s}\phi(s-s')u_{xs'}|_{x=1}\,\mathrm{d}s' = 0 \qquad \text{(V.13)}$$

$$u|_{x=0} + k_0\int_{-\infty}^{s}\phi(s-s')u_{s'}|_{x=0}\,\mathrm{d}s' = g(s) \qquad \text{(V.14)}$$

Here

$$k_0 = \frac{D'}{D} = \frac{\bar{V}_1G_0}{RT}\rho_1\hat{V}_1 \qquad \text{(V.15)}$$

according to eq IV.26 and V.8. Equations V.3, V.5, and V.10 can be expressed

$$k_1u_{ss} + u_s = u_{xx} + k_2u_{xxs} \qquad \text{(V.16)}$$

$$u_s|_{x=0} + k_3u|_{x=0} = k_3g(s) + k_1k_3g'(s) \qquad \text{(V.17)}$$

and

$$u_x|_{x=1} + k_2 u_{xs}|_{x=1} = 0 \qquad \text{(V.18)}$$

respectively. Here

$$k_1 = \tau D/l^2 \qquad \text{(V.19)}$$

is the diffusion Deborah number

$$k_2 = \frac{\tau}{l^2}(D + D') \qquad \text{(V.20)}$$

and

$$k_3 = 1/k_2 \qquad \text{(V.21)}$$

In the above

$$D' = \frac{D\bar{V}_1}{RT}\rho_1 \hat{V}_1 \frac{\eta}{\tau} \qquad \text{(V.22)}$$

according to eq IV.26, V.2b, and V.8.

Equations V.12–V.14 can be solved numerically for any reasonable function $\phi(s-s')$. Equations V.16–V.18 are solved analytically in the next section. The results from either procedure allow the prediction of the dimensionless mass of solvent in the solution

$$W(s) = \frac{M(t)}{KAl} - \frac{a^-}{A} = \int_0^1 u(x,s)\,\mathrm{d}x \qquad \text{(V.23)}$$

VI. Analytical Solutions

1. General Solution. The initial value problem (V.16)–(V.18) submits to analytical solution by variation of parameters.[16] A general solution is developed in Appendix D for sorption with an arbitrary time dependence $g(t)$ in the external activity (see eq II.2). We specialize the general solution below to two important cases.

2. Classical Sorption. In the case of a small-amplitude step in the external solvent activity, $g(t) = H(t)$ and we have

$$u(0,s) = h(s) = 1 + (k_1k_3 - 1)e^{-k_3 s} \qquad \text{(VI.1)}$$

and the general solution (D.11) becomes

$$u(x,s) = 1 + (k_1k_3 - 1)e^{-k_3 s} + \sum_{i=1}^{3}\sum_{n=0}^{\infty} C_n{}^i e^{-\phi_n{}^i s} \qquad \text{(VI.2)}$$

where

$$C_n{}^1 = \frac{1}{\lambda_n\beta_n}\left[-k_1k_3(\alpha_n + \beta_n) + k_3(k_1k_3 - 1) + \frac{k_3}{k_1}\frac{(k_1k_3 - 1)^2}{(\alpha_n - \beta_n - k_3)} \right] \qquad \text{(VI.2a)}$$

$$C_n{}^2 = \frac{1}{\lambda_n\beta_n}\left[k_1k_3(\alpha_n - \beta_n) - k_3(k_1k_3 - 1) - \frac{k_3}{k_1}\frac{(k_1k_3 - 1)^2}{(\alpha_n + \beta_n - k_3)} \right] \qquad \text{(VI.2b)}$$

and

$$C_n{}^3 = \frac{1}{\lambda_n\beta_n}\frac{k_3}{k_1}(k_1k_3 - 1)^2\left[\frac{1}{(\alpha_n + \beta_n - k_3)} - \frac{1}{(\alpha_n - \beta_n - k_3)} \right] \qquad \text{(VI.2c)}$$

Also

$$\phi_n{}^1 = \alpha_n - \beta_n \qquad \text{(VI.2d)}$$

$$\phi_n{}^2 = \alpha_n + \beta_n \qquad \text{(VI.2e)}$$

with α_n and β_n defined by eq D.9b and D.9c and

$$\phi_n{}^3 = k_3 \qquad \text{(VI.2f)}$$

Integration of (VI.2) over x gives

$$W(s) = 1 + (k_1k_3 - 1)e^{-k_3 s} + \sum_{i=1}^{3}\sum_{n=0}^{\infty} \frac{2C_n{}^i}{\lambda_n} e^{-\phi_n{}^i s} \qquad \text{(VI.3)}$$

for the dimensionless mass of solvent absorbed during sorption.

3. Oscillatory Sorption. In light of the recent efforts of Vrentas, Duda, and co-workers[6] we evaluated $W(s)$ when $g(s) = \sin ws$, with $w = \omega l^2/D$ being a dimensionless driving frequency. We consider only the steady periodic solution, $W^{\mathrm{p}}(s)$. For sinusoidal $g(s)$, the steady periodic response is sinusoidal, with a phase, $y^{\mathrm{W}}(w)$, and amplitude, $Y^{\mathrm{W}}(w)$, depending on the driving frequency, w

$$W^{\mathrm{p}}(s) = Y^{\mathrm{W}}(w)\sin(ws + y^{\mathrm{W}}(w)) \qquad \text{(VI.4)}$$

The method used by Carslaw and Jaeger[17] can be applied to develop $y^{\mathrm{W}}(w)$ and $Y^{\mathrm{W}}(w)$ from (V.16)–(V.18) without difficulty; details of the derivation appear in Appendix E.

VII. Predictions

1. Special Cases. Asymptotic behaviors predicted by the theory can be discerned by careful inspection of the steady periodic solutions for $y^{\mathrm{W}}(w)$ and $Y^{\mathrm{W}}(w)$ (eq E-8 and E-9).

In the limit of a very rapid rheological response, i.e., $k_1 \to 0$ and $k_2 \to 0$, the results reduce to the classical expressions.[17] This agrees with the Deborah number correlation of Vrentas and Duda.[4,5]

Another special case occurs when $k_1k_3 \to 1$ which implies $k_2 \to k_1$. The definitions of k_1 and k_2 show that $D' \to 0$ in this case. Physically, this corresponds to (a) a solvent with an extremely small molar volume ($\hat{V}_1 \to 0$), (b) a polymer component with a very small instantaneous modulus ($G_0 \to 0$), or (c) the limit of trace diffusion in the pure polymer ($\rho_1\hat{V}_1 \to 0$). Inspection shows that the classical behavior is again recovered; the same conclusion is obvious from eq V.12–V.14.

2. Numerical Study. Further study of the behavior predicted by the theory requires numerical evaluation. In earlier work, Durning[2] evaluated k_1 and k_2 over a range of solvent weight fraction in the semidilute and concentrated region for poly(methyl methacrylate)/methyl acetate at 30 °C; it was found $(k_2/k_1 - 1) = D'/D \cong 3$ over a wide range. We expect that D'/D varies slowly with the solvent weight fraction in most semidilute and concentrated systems but the magnitude varies from system to system. Accordingly, the numerical study varies the Deborah number, k_1, with $(k_2/k_1 - 1)$ held constant, complemented by a variation in $(k_2/k_1 - 1)$ with k_1 held constant.

Figure 3 shows the response for $k_1 > 1$ with $(k_2/k_1 - 1) = 3$. At high dimensionless frequencies ($w > 5$) the phase angle, $y^{\mathrm{W}}(w)$, approaches the classical prediction, although the amplitude is severely attenuated, which probably precludes accurate experimental observation in this region. At lower frequencies, a deviation from the classical response appears, which reflects the viscoelastic transport expected for $k_1 \sim \mathcal{O}(1)$. A distinct peaked excursion from the classical curve is the dominant feature (demarked by arrows in Figure 3); the dimensionless frequency locating the peak, w^*, becomes smaller as the Deborah number increases. A strong analogy exists between the predicted phase angle behavior and that observed in the dynamic mechanical testing of polymers in so far as w^* represents a "resonant frequency" of the polymer solution under the

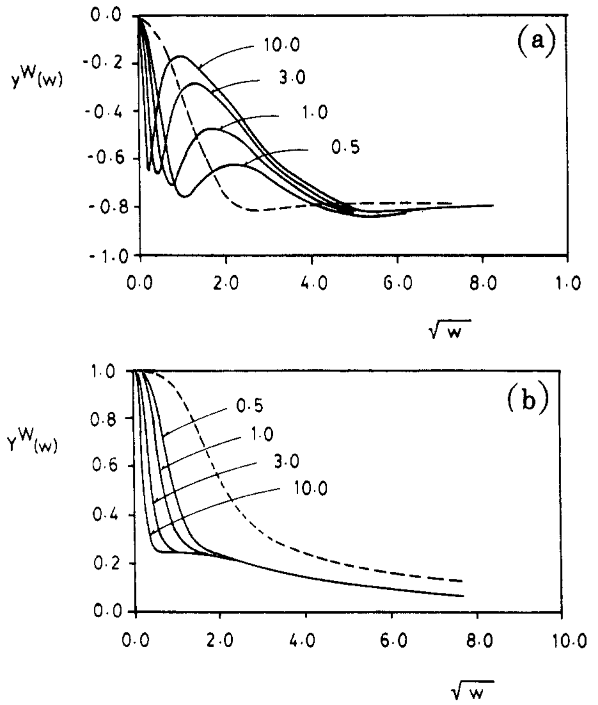

Figure 3. (a) Effect of the diffusion Deborah number for values $\mathcal{O}(1)$ and larger on the frequency dependence of the phase angle $y^W(w)$ with $(k_2/k_1 - 1) = 3$. The dashed line represents the classical prediction; Deborah numbers are indicated. (b) Effect of the diffusion Deborah number for values $\mathcal{O}(1)$ and larger on the frequency dependence of the amplitude $Y^W(w)$ with $(k_2/k_1 - 1) = 3$. The dashed line represents the classical prediction; Deborah numbers are indicated.

oscillatory stressor of a modulating external activity. Since the amplitude in the low-frequency region remains relatively large, experimental observation of this interesting behavior appears possible provided the actual frequency $\omega = wD/l^2$ is not too small.

Figure 4, parts a and b, show the response for small Deborah numbers ($^1/_{10} < k_1 < {}^1/_{1000}$). In the low-frequency region, the behavior is nearly classical, which agrees with expectations based on the Deborah number correlation.[4,5] Interestingly, the "resonance" peaks still appear in the high-frequency region, the resonant frequency occurring at higher values for smaller Deborah numbers. The peaked excursions from the classical behavior appear more clearly in Figure 4c, where the abscissa is $w^{-1/2}$. Unfortunately, the amplitude in the high-frequency range is attenuated, which probably precludes accurate observation of the interesting behavior at small Deborah numbers.

Figure 5 shows the effect on the phase angle response of a variation in $(k_2/k_1 - 1)$ for $k_1 = 1$. The calculations reveal that the magnitude of the deviation from the classical response depends very much on the value of $(k_2/k_1 - 1)$. As $(k_2/k_1 - 1)$ becomes smaller, the resonance peak is reduced and the response approaches the classical behavior. The limit $(k_2/k_1 - 1) \to 0$ is the second special case discussed earlier.

3. Comparison with Experiment. A satisfying comparison of the predictions for classical sorption (eq VI.3) with data on the poly(methyl methacrylate)/methyl acetate system is presented elsewhere.[2]

Measurements of the phase angle response, $y^W(w)$, for the system poly(vinyl acetate) (PVAc)/water (H_2O) near the glass transition have been performed recently;[18] details of the apparatus, materials, and data reduction procedures can be found in ref 6. The data for a polymer with a weight-average molecular weight of 230000 are summarized in Table I. The dimensionless frequencies were calculated from the dry polymer film thickness and the mutual diffusion coefficients measured by Kishimoto et al.[19]

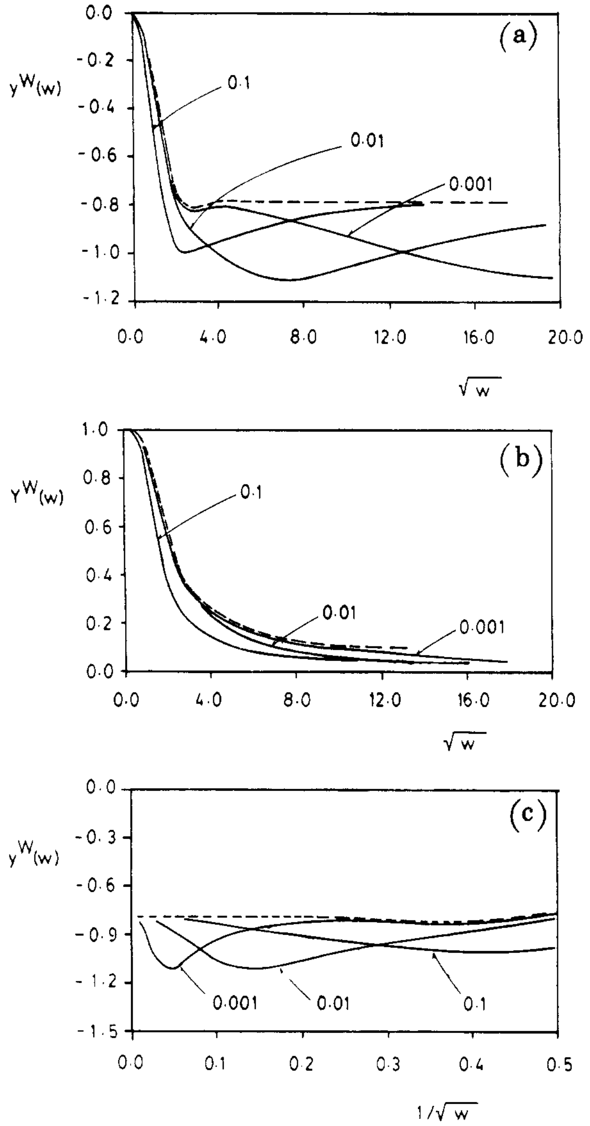

Figure 4. (a) Effect of the diffusion Deborah number for small values on the frequency dependence of the phase angle $y^W(w)$ with $(k_2/k_1 - 1) = 3$. The dashed line represents the classical prediction; Deborah numbers are indicated. (b) Effect of the diffusion Deborah number for small values on the frequency dependence of the amplitude $Y^W(w)$ with $(k_2/k_1 - 1) = 3$. The dashed line represents the classical prediction; Deborah numbers are indicated. (c) Replot of (a) with $w^{-1/2}$ for the abscissa.

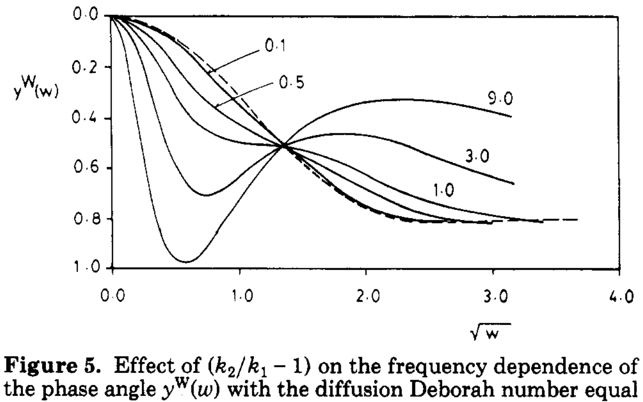

Figure 5. Effect of $(k_2/k_1 - 1)$ on the frequency dependence of the phase angle $y^W(w)$ with the diffusion Deborah number equal to 1. The dashed line represents the classical prediction; values of $(k_2/k_1 - 1)$ are indicated.

A direct comparison between the theory and the data requires the evaluation at the experimental conditions of

Table I
Phase Angle, $y^W(w)$, vs. Dimensionless Frequency for the PVAc/H_2O System[a]

temp, °C	mass fraction $H_2O \times 10^3$ [b]	$w^{1/2}$	$y^W(w)$
35	9.7	1.61	−0.53
35	9.0	1.14	−0.40
35	9.2	0.80	−0.32
45	9.4	1.05	−0.41
45	9.2	0.74	−0.31
45	8.6	0.52	−0.24
45	8.6	0.43	−0.21
45	8.6	0.37	−0.20
50	8.1	0.93	−0.45
50	8.1	0.66	−0.25
50	8.1	0.47	−0.16
50	8.1	0.38	−0.14

[a] Data reported in ref 18. [b] Computed from the average partial pressure of H_2O by using the equilibrium isotherm reported in ref 18 and by assuming constant partial specific volumes.

Table II
Free Volume Constants for PVAc

constant	value[a]
K_{12}/γ	4.33×10^{-4} cm^3/(g·K)
$K_{22} - T_g^{(2)}$	−256 K
$\hat{V}_2^*$	0.728 cm^3/g

[a] Reported in ref 18.

η and τ contained in k_1, k_2, and $k_3 = 1/k_2$. We associate η and τ with

$$\tau = \int_{-\infty}^{\infty} \tau' H(\tau')\ \mathrm{d}\ln \tau' \Big/ \int_{-\infty}^{\infty} H(\tau')\ \mathrm{d}\ln \tau' = \eta/G_0 \tag{VII.1}$$

where $H(\tau)$ is the relaxation spectrum of the mixture, η is its zero shear viscosity, and G_0 is its instantaneous shear modulus.

The values of η and τ under the experimental conditions were calculated from the pure polymer shear response using viscoelastic superposition. The zero-shear viscosities reported by Ninomiya and Ferry[20] give $\eta = 10^{10}$ P for the pure polymer at 75 °C when the correction for molecular weight discussed by Berry and Fox[21] is applied. Values of η at the experimental temperatures were deduced from the Vrentas–Duda free volume theory[22]

$$\ln \frac{\eta(T)}{\eta(T_0)} = \gamma \hat{V}_2^* \left[\frac{1}{\hat{V}_{FH}(T)} - \frac{1}{\hat{V}_{FH}(T_0)} \right] \tag{VII.2}$$

with

$$\frac{\hat{V}_{FH}(T)}{\gamma} = \frac{K_{12}}{\gamma}[K_{22} + T - T_g^{(2)}] \tag{VII.2a}$$

being the effective specific free volume. The constants K_{12}/γ and $K_{22} - T_g^{(2)}$ are related to the WLF constants for the polymer, and $\hat{V}_2^*$ means the specific hard-core volume of the chain; Table II summarizes the values used. The pure polymer viscosities were corrected for the presence of water by using the concentration shift factors measured by Fujita and Kishimoto.[23]

The relaxation times were computed from the viscosities according to (VII.1) with G_0 determined from

$$G_0 = \lim_{\omega \to \infty} G'(\omega) \tag{VII.3}$$

where $G'(\omega)$ means the shear storage modulus at the frequency ω. We used the value reported by Kovacs, Stratton, and Ferry[24] for pure PVAc at 35 °C with a weight-average molecular weight of 2×10^6 without further correction.

Table III
Diffusion Deborah Numbers for the Conditions in Table I

temp, °C	k_1
35	3.4
45	0.04
50	0.005

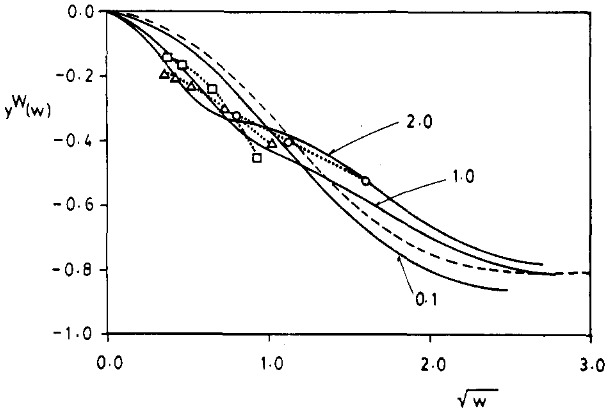

Figure 6. Comparison of theory (eq VI.22) with oscillatory sorption data (Table I) for the system poly(vinyl acetate)/water at 35 °C (○), 45 °C (△), and 50 °C (□). The dashed line represents the classical predictions; values of k_1 are indicated.

The viscosities and relaxation times together with the mutual diffusion coefficients reported by Kishimoto give the diffusion Deborah numbers summarized in Table III. We found $(k_2/k_1 - 1) = 0.2$.

Figure 6 shows the comparison between the theory and the data. The calculations were done with $(k_2/k_1 - 1) = 0.5$ for a range of Deborah numbers near 1. The agreement of the data at 35 °C with the predictions for $k_1 = 2.0$ is good. In light of Figure 5, we feel it is notable that both the data and theory cut the classical curve at the same position and angle.

At higher temperatures, the data should match the predictions with Deborah numbers in the range 0.05–0.005, but the agreement is more satisfactory for k_1 in the range 1–0.1. The large values of k_1 needed to match the data may reflect errors in the diffusion coefficients reported by Kishimoto et al.[19] The values at 45 and 50 °C were determined by sorption/desorption methods which would be spuriously low if influenced by viscoelastic effects. This would move the data in these cases to the right in Figure 6, improving the agreement. It is also possible that more than one relaxation time is needed to properly characterize the rheology of the polymer component; in effect multiple Deborah numbers may exist. This effect could be handled by eq V.12–V14 with an appropriate relaxation function, although analytical treatment would be difficult.

Given that (a) the present theory includes several approximations needed for analytical results, and (b) the data represent preliminary measurements, the agreement displayed in Figure 6 seems satisfactory.

VIII. Conclusions

Fick's law cannot adequately describe mutual diffusion in concentrated polymer solutions. The reason is easily understood. The interdiffusion of polymer and solvent deforms the polymer component and stores free energy temporarily in the polymer structure; under certain circumstances this stored free energy makes an important contribution to the driving force for the process.

For small driving forces, the transient network and reptation models lead to a simple expression for the solvent flux (eq IV.25) containing a memory integral associated with the deformation of the polymer structure. The flux yields a linear integrodifferential equation for the unsteady solvent mass balance (eq V.1). Only the mutual diffusion coefficient, the rheological properties of the polymer component and common state properties of the components appear in the theory.

With the approximation that the polymer component behaves like a Maxwell fluid, analytical formulas for measurable quantities can be derived. The approximate theory predicts non-Fickian behavior, in reasonable agreement with data from classical and oscillatory sorption experiments. The theory shows that deviations from Fick's law appear when the diffusion Deborah number is about 1.

The analysis of oscillatory sorption clarifies its potential value: in the study of mutual diffusion the method seems analogous to dynamic mechanical testing in the study of polymer rheology. Hopefully, additional experimental work along these lines will be forthcoming.

It remains to extend the theory presented here to the case of large driving forces.

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Appendix A

A reasonable expression for $\mathbf{j}_1{}^2$ must ensure the inequality (III.3). For a nonreactive binary mixture, a differential balance on entropy gives

$$\sigma = \rho\frac{D}{Dt}\hat{\P} + \frac{\partial}{\partial\mathbf{r}}\cdot\eta + \rho\frac{Q}{T} \geq 0 \qquad \text{(A.1)}$$

where $\hat{\P}$ means the specific entropy, η means the entropy flux, Q means the radiative heating, and D/Dt means the barycentric derivative. The entropy flux (IV.1), the relation $\mathbf{J}_1 + \mathbf{J}_2 = 0$, and the equation of energy for the mixture allow the representation

$$\rho\frac{D}{Dt}\hat{\Gamma} + \rho\hat{\P}\frac{DT}{Dt} + \mathbf{\Pi}:\frac{\partial}{\partial\mathbf{r}}\mathbf{v} + \left(\frac{\mathbf{q}}{T}\right)\cdot\frac{\partial}{\partial\mathbf{r}}T + \Delta\frac{\partial}{\partial\mathbf{r}}\cdot\mathbf{J}_1 + T\mathbf{J}_1\cdot\frac{\partial}{\partial\mathbf{r}}\left(\frac{\Delta}{T}\right) \leq 0 \qquad \text{(A.2)}$$

for (A.1). Here, $\mathbf{\Pi}$ is the pressure tensor and Δ means $\rho[((\partial/\partial\rho_1)\hat{\Gamma})_{\rho_2,T,\{\alpha\}} - ((\partial/\partial\rho_2)\hat{\Gamma})_{\rho_1,T,\{\alpha\}}]$ with $\{\alpha\}$ being the set of arguments influencing $\hat{\Gamma}$ other than composition and temperature.

For a polymer solution we presume a frame-indifferent constitutive relation

$$\hat{\Gamma} = \hat{\Gamma}(\rho_1,\rho_2,T,\mathbf{E}^{(2)};T(s),\mathbf{E}^{(2)}(s)) \qquad \text{(A.3)}$$

where $\mathbf{E}^{(2)}$ is the displacement gradient for the polymer phase and the functions $T(s)$ and $\mathbf{E}^{(2)}(s)$ describe the history of T and $\mathbf{E}^{(2)}$, respectively; note the set $\{\alpha\}$ contains $\mathbf{E}^{(2)}$, $T(s)$, and $\mathbf{E}^{(2)}(s)$. Expanding $D\hat{\Gamma}/Dt$ and using the species continuity equation lead to

$$\rho\left[\left(\frac{\partial}{\partial T}\hat{\Gamma}\right) + \hat{\P}\right]\frac{DT}{Dt} + \mathbf{F}:\frac{D}{Dt}\mathbf{E}^{(2)} + \left(\frac{\mathbf{q}}{T}\right)\cdot\frac{\partial}{\partial\mathbf{r}}T + T\mathbf{J}_1\cdot\frac{\partial}{\partial\mathbf{r}}\left(\frac{\Delta}{T}\right) + \rho\delta\hat{\Gamma} \leq 0 \qquad \text{(A.4a)}$$

where

$$\mathbf{F} = \left(\frac{\partial}{\partial\mathbf{E}^{(2)}}\hat{\Gamma}\right)^{\dagger} + (\mathbf{E}^{(2)})^{-1}\cdot\left\{\mathbf{\Pi} - \rho\left[\rho_1\left(\frac{\partial}{\partial\rho_1}\hat{\Gamma}\right) + \rho_2\left(\frac{\partial}{\partial\rho_2}\hat{\Gamma}\right)\right]\delta\right\} \qquad \text{(A.4b)}$$

and $\delta\hat{\Gamma}$ means the Frechet expansion of $\hat{\Gamma}$ in the function arguments. (It is understood that appropriate arguments are held constant for the partial differentiations.)

To satisfy (A.4a) identically for every isothermal kinetic process the conditions

$$\mathbf{J}_1\cdot\frac{\partial}{\partial\mathbf{r}}\Delta \leq 0 \qquad \text{(A.5a)}$$

$$\mathbf{F} = 0 \qquad \text{(A.5b)}$$

and

$$\delta\hat{\Gamma} \leq 0 \qquad \text{(A.5c)}$$

are needed. The first can be satisfied by picking $\mathbf{J}_1 = -\Omega(\partial/\partial\mathbf{r})\Delta$, with Ω being a positive scalar coefficient, possibly depending on the composition and the invariants of $\mathbf{E}^{(2)}$ and $\mathbf{E}^{(2)}(s)$. The second condition (A.5b) provides a relation between the specific free energy $\hat{\Gamma}$ and the flow-dependent part of the pressure tensor, $\mathbf{\Pi} - P\delta$ where $P = \rho[\rho_1((\partial/\partial\rho_1)\hat{\Gamma})_{\rho_2,T,\{\alpha\}} + \rho_2((\partial/\partial\rho_2)\hat{\Gamma})_{\rho_1,T,\{\alpha\}}]$ is the thermodynamic pressure.[8c] The condition (A.5c) imposes restrictions on the dependence of $\hat{\Gamma}$ on the strain history $\mathbf{E}^{(2)}(s)$.

Appendix B

Equivalant expressions of the constitutive behavior in eq A.3 are

$$\hat{\Gamma} = \hat{\Gamma}(\omega_1,\hat{V},T,\mathbf{E}^{(2)};T(s),\mathbf{E}^{(2)}(s)) \qquad \text{(B.1a)}$$

and

$$\check{\Gamma} = \check{\Gamma}(\rho_1,\rho_2,T,\mathbf{E}^{(2)};T(s),\mathbf{E}^{(2)}(s)) \qquad \text{(B.1b)}$$

The requirement that these be consistent with (A.3) implies a generalized Gibbs–Duhem equation.

Expanding (B.1a) leads to

$$\mathrm{d}\hat{\Gamma} = -\hat{\P}\,\mathrm{d}T - P\,\mathrm{d}\hat{V} + \Delta\,\mathrm{d}\omega_1 + \left(\frac{\partial}{\partial\mathbf{E}^{(2)}}\hat{\Gamma}\right)^{\dagger}:\mathrm{d}\mathbf{E}^{(2)} + \delta\hat{\Gamma} \qquad \text{(B.2a)}$$

where the relations

$$-\hat{\P} = \frac{\partial}{\partial T}\hat{\Gamma} \qquad \text{(B.3a)}$$

$$P = \rho\left[\rho_1\left(\frac{\partial}{\partial\rho_1}\hat{\Gamma}\right)_{\rho_2,T,\{\alpha\}} + \rho_2\left(\frac{\partial}{\partial\rho_2}\hat{\Gamma}\right)_{\rho_1,T,\{\alpha\}}\right] = -\left(\frac{\partial}{\partial\hat{V}}\hat{\Gamma}\right) \qquad \text{(B.3b)}$$

and

$$\Delta = \rho\left[\left(\frac{\partial}{\partial\rho_1}\hat{\Gamma}\right)_{\rho_2,T,\{\alpha\}} - \left(\frac{\partial}{\partial\rho_2}\hat{\Gamma}\right)_{\rho_1,T,\{\alpha\}}\right] = \left(\frac{\partial}{\partial\omega_1}\hat{\Gamma}\right) \qquad \text{(B.3c)}$$

have been used. Equation B.3a is required by the inequality (A.4a); eq B.3b and B.3c follow from a comparison between the expansions of (A.3) and (B.1a). In eq B.2a, $\delta\hat{\Gamma}$ means the Frechet expansion of $\hat{\Gamma}$ in the function arguments. (In the above and in the relations that follow, it is understood that appropriate arguments are held constant for the partial differentiations.)

In view of the connection $\check{\Gamma} = \hat{\Gamma}/\hat{V}$, an expansion of eq B.1b gives

$$\hat{\Gamma} = -\hat{V}P + \omega_1\left(\frac{\partial}{\partial\rho_1}\check{\Gamma}\right) + \omega_2\left(\frac{\partial}{\partial\rho_2}\check{\Gamma}\right) \quad \text{(B.4a)}$$

and

$$\Delta = \left(\frac{\partial}{\partial\rho_1}\check{\Gamma}\right) - \left(\frac{\partial}{\partial\rho_2}\check{\Gamma}\right) \quad \text{(B.4b)}$$

after comparison with eq B.2a. Equation B.4a ensures Euler's theorum for the extensive thermodynamic functions at equilibrium.

Expanding eq B.4a and subtracting the result from eq B.2a give a Gibbs–Duhem relation for the fluid mixture obeying (A.3)

$$0 = -\hat{¶}\,\mathrm{d}T + \hat{V}\,\mathrm{d}P - \omega_1\,\mathrm{d}\left(\frac{\partial}{\partial\rho_1}\hat{\Gamma}\right) - \omega_2\,\mathrm{d}\left(\frac{\partial}{\partial\rho_2}\hat{\Gamma}\right) + \left(\frac{\partial}{\partial\mathbf{E}^{(2)}}\hat{\Gamma}\right)^{\dagger}:\mathrm{d}\mathbf{E}^{(2)} + \delta\hat{\Gamma} \quad \text{(B.5)}$$

For isothermal diffusion at constant pressure, the first two terms on the right in (B.5) vanish. Also, for diffusion under a small driving force the components of the displacement gradient $\mathbf{E}^{(2)}$ are infinitesimal, making the last two terms on the right vanishingly small. Under these conditions, (B.5) provides

$$\frac{\partial}{\partial\mathbf{r}}\rho\left(\frac{\partial}{\partial\rho_1}\hat{\Gamma}\right)_{\rho_2,T,\{\alpha\}} = -\frac{\omega_2}{\omega_1}\frac{\partial}{\partial\mathbf{r}}\rho\left(\frac{\partial}{\partial\rho_2}\hat{\Gamma}\right)_{\rho_1,T,\{\alpha\}} \quad \text{(B.6)}$$

Appendix C

The polymer continuity equation gives the z velocity gradient of the polymer phase, $\partial v_z^{(2)}/\partial z$, as in eq IV.23. The polymer fixed coordinate is defined by

$$\left(\frac{\partial}{\partial z}\xi\right)_t = \rho_2\hat{V}_2 \quad \text{(C.1)}$$

and the transformation of $(\partial\rho_2/\partial t)_z$ is

$$\left(\frac{\partial}{\partial t}\rho_2\right)_z = \left(\frac{\partial}{\partial t}\rho_2\right)_\xi + \left(\frac{\partial}{\partial t}\xi\right)_z\left(\frac{\partial}{\partial\xi}\rho_2\right)_t \quad \text{(C.2)}$$

Expanding (IV.23) and using (C.2) give

$$\left(\frac{\partial}{\partial z}v_z^{(2)}\right)_t = -\frac{1}{\rho_2\hat{V}_2}\left(\frac{\partial}{\partial z}\left(\frac{\partial}{\partial t}\xi\right)_z\right)_t + \frac{1}{(\rho_2\hat{V}_2)^2}\left(\frac{\partial}{\partial z}\rho_2\hat{V}_2\right)_t\left(\frac{\partial}{\partial t}\xi\right)_z \quad \text{(C.3)}$$

where the partial specific volume $\hat{V}_2$ is considered constant. Reversing the order of differentiation in the first term on the right and using (C.1) and (C.2) provide

$$\left(\frac{\partial}{\partial z}v_z^{(2)}\right)_t = -\frac{1}{\rho_2\hat{V}_2}\left[\left(\frac{\partial}{\partial t}\rho_2\hat{V}_2\right)_\xi + \left(\frac{\partial}{\partial t}\xi\right)_z\left(\frac{\partial}{\partial\xi}\rho_2\hat{V}_2\right)_t\right] + \frac{1}{(\rho_2\hat{V}_2)^2}\left(\frac{\partial}{\partial z}\rho_2\hat{V}_2\right)_t\left(\frac{\partial}{\partial t}\xi\right)_z \quad \text{(C.4)}$$

Transforming the partial derivative in z in the second term on the right to the polymer fixed coordinate gives

$$\frac{\partial v_z^{(2)}}{\partial z} = \hat{V}_1(\rho_2\hat{V}_2)\left(\frac{\partial C}{\partial t}\right)_\xi \quad \text{(C.5)}$$

where the relation $\rho_1\hat{V}_1 + \rho_2\hat{V}_2 = 1$ has been used.

Appendix D

An analytical solution to (V.16)–(V.18) can be developed by variation of parameters.[16] The initial state of the system is for $0 < x < 1$

$$u(x,0) = 0 \quad \text{(D.1a)}$$

$$u_s(x,0) = 0 \quad \text{(D.1b)}$$

The second condition follows from the definition of μ_1 (eq IV.14) and the fact that the solution is initially at rest.

The boundary condition at the solution/vapor interface can be restated as

$$u(0,s) = h(s) \quad \text{(D.2)}$$

where $h(s)$ is the solution to the ordinary differential equation (V.18) with $u(x{=}0,s{=}0) = 0$.

Defining

$$u(x,s) = h(s) + v(x,s) \quad \text{(D.3)}$$

leads to an initial value problem for v with homogeneous boundary conditions

$$k_1v_{ss} + v_s + v_{xx} - k_2v_{xxs} = -k_1h''(s) - h'(s) \quad \text{(D.4a)}$$

$$v(x{=}0,s) = 0 \quad \text{(D.4b)}$$

$$k_2v_{xs}(x{=}1,s) + v_x(x{=}1,s) = 0 \quad \text{(D.4c)}$$

$$v(x,s{=}0) = -h(0) \quad \text{(D.4d)}$$

$$v_s(x,s{=}0) = h'(0) \quad \text{(D.4e)}$$

The homogeneous form of (D.4a) suggests the solution

$$v(x,s) = \sum_{n=0}^{\infty} b_n(s)\sin\lambda_n x \quad \text{(D.5a)}$$

where

$$\lambda_n = (n + \tfrac{1}{2})\pi \quad \text{(D.5b)}$$

The orthogonality of the sin $\lambda_n x$ provides

$$2\int_0^1 v(x,s)\sin\lambda_n x\,\mathrm{d}x = b_n(s) \quad \text{(D.6)}$$

so that multiplication of (D.4a) by sin $\lambda_n x$ followed by integration over x leads to

$$k_1b_n''(s) + b_n'(s) = 2\int_0^1 (k_2v_{xxs} + v_{xx})\,\mathrm{d}x - \frac{2}{\lambda_n}(k_1h''(s) + h'(s)) \quad \text{(D.7)}$$

Carrying out the integrations by parts leads to inhomogeneous, ordinary differential equations for the $b_n(s)$, which are solved by variation of parameters to give

$$b_n(s) = b_n^{\mathrm{h}}(s) + b_n^{\mathrm{p}}(s) \quad \text{(D.8)}$$

The homogeneous solution, $b_n^{\mathrm{h}}(s)$, is

$$b_n^{\mathrm{h}}(s) = A_ne^{-(\alpha_n-\beta_n)s} + B_ne^{-(\alpha_n+\beta_n)s} \quad \text{(D.9a)}$$

with

$$\alpha_n = \left(\frac{1 + \lambda_n^2k_2}{2k_1}\right) \quad \text{(D.9b)}$$

and

$$\beta_n = +\frac{1}{2}\left[\left(\frac{1 + \lambda_n^2k_2}{k_1}\right)^2 - \frac{4\lambda_n^2}{k_1}\right]^{1/2} \quad \text{(D.9c)}$$

The A_n and B_n are constants to be determined from the initial conditions (D.4d) and (D.4e). The particular solution, $b_n^{\mathrm{p}}(s)$, is

$$b_n^{\mathrm{p}}(s) = \frac{1}{\beta_n\lambda_n}\int_0^s [e^{-(\alpha_n+b_n)(s-s')} - e^{-(\alpha_n-\beta_n)(s-s')}]\frac{k_1h''(s') + h'(s')}{k_1}\,\mathrm{d}s' \quad \text{(D.10)}$$

Equations D.3, D.4d, D.4e, D.5, and D.8–D.10 lead to a general solution for $u(x,s)$ during one-dimensional sorption under a small driving force

$$u(x,s) = h(s) + \Sigma^{(1)} + \Sigma^{(2)} \tag{D.11}$$

with

$$\Sigma^{(1)} = \sum_{n=0}^{\infty} \frac{\sin \lambda_n x}{\lambda_n \beta_n}\{[h'(0) + h(0) \times (\alpha_n - \beta_n)]e^{-(\alpha_n+\beta_n)s} - [h'(0) + h(0)(\alpha_n + \beta_n)]e^{-(\alpha_n-\beta_n)s}\} \tag{D.11a}$$

and

$$\Sigma^{(2)} = \sum_{n=0}^{\infty} \frac{\sin \lambda_n x}{\lambda_n \beta_n}\left\{\int_0^s e^{-(\alpha_n-\beta_n)(s-s')} \times \left[\frac{k_1 h''(s') + h'(s')}{k_1}\right] \mathrm{d}s' + \int_0^s e^{-(\alpha_n+\beta_n)(s-s')}\left[\frac{k_1 h''(s') + h'(s')}{k_1}\right] \mathrm{d}s'\right\} \tag{D.11b}$$

Appendix E

The method of Carslaw and Jeager[17] can be used to develop the steady periodic solution of (V.16)–(V.18) when $g(s) = \sin ws$. Integration of the boundary condition (V.18) for $g(s) = \sin ws$ gives

$$u(0,s) = h(s) = D \sin ws + E \cos ws - Ee^{-k_3 s} \tag{E.1}$$

where

$$D = k_3(k_3 + k_1 w^2)/(k_3^2 + w^2) \tag{E.1a}$$

and

$$E = -k_3 w(1 - k_1 k_3)/(k_3^2 + w^2) \tag{E.1b}$$

Only the first two terms on the right in (E.1) need to be considered when developing the steady periodic solution.

The periodic behavior follows from the general solution (D.11) by first letting

$$h(s) = Fe^{as} \tag{E.2}$$

This gives the solution

$$u(x,s) = u_1(x,s) + u_2(x,s) \tag{E.3}$$

where

$$u_1(x,s) = Fe^{as}\,\frac{\cosh \sigma(x-1)}{\cosh \sigma} \tag{E.4}$$

with

$$\sigma^2 = \frac{a(k_1 a + 1)}{(k_2 a + 1)} \tag{E.5}$$

leads to the periodic part and $u_2(x,s)$ corresponds to irrelevant, transient portions of $u(x,s)$.

In view of (E.1) the measurable quantity $W^{p}(s)$ can be expressed

$$W^{p}(s) = \mathrm{Im}\left[\int_0^1 u_1(x,s;F,a)\,\mathrm{d}x\right]_{\substack{F=D\\a=jw}} + \mathrm{Re}\left[\int_0^1 u_1(x,s;F,a)\,\mathrm{d}x\right]_{\substack{F=E\\a=jw}} \tag{E.6}$$

where Im and Re mean the real and imaginary parts of the argument, respectively, and $j = (-1)^{1/2}$. The notation $u_1(x,s;F,a)$ emphasizes the dependences on the parameters F and a, while the inferior symbols indicate the appropriate values of each.

Evaluation of (E.6) leads to

$$W^{p}(s) = Y^{W}(w) \sin (ws + y^{W}(w)) \tag{E.7}$$

where

$$Y^{W}(w) = L(w)\frac{(\sinh^2 2\alpha + \sin^2 2\beta)^{1/2}}{(\cosh 2\alpha + \cos 2\beta)} \tag{E.8}$$

with

$$L(w) = \left[\frac{k_3^2 + (k_1 k_3 w)^2}{w(k_3^2 + w^2)}\right]^{1/2}\left[\frac{(k_2 w)^2 + 1}{(k_1 w)^2 + 1}\right]^{1/4} \tag{E.8a}$$

and

$$y^{W}(w) = \tan^{-1} y_1^{W}(w) - \tan^{-1} y_2^{W}(w) \tag{E.9}$$

with

$$y_1^{W}(w) = \frac{\alpha \sin 2\beta - \beta \sinh 2\alpha}{\beta \sin 2\beta + \alpha \sinh 2\alpha} \tag{E.9a}$$

and

$$y_2^{W}(w) = \frac{w(1 - k_1 k_3)}{k_3 + k_1 w^2} \tag{E.9b}$$

Here

$$\alpha = w^{1/2}\left(\frac{(k_1 w)^2 + 1}{(k_2 w)^2 + 1}\right)^{1/4} \cos\left[\tfrac{1}{2} \tan^{-1}\left(\frac{k_1 k_2 w^2 + 1}{(k_2 - k_1)w}\right)\right] \tag{E.10a}$$

and

$$\beta = w^{1/2}\left(\frac{(k_1 w)^2 + 1}{(k_2 w)^2 + 1}\right)^{1/4} \sin\left[\tfrac{1}{2} \tan^{-1}\left(\frac{k_1 k_2 w^2 + 1}{(k_2 - k_1)w}\right)\right] \tag{E.10b}$$

are the real and imaginary parts of σ for $a = jw$, respectively.

Important Symbols

$a(t)$	solvent activity in the vapor phase.
a^{-}	initial solvent activity in the vapor phase.
a'	solvent activity in solution.
A	amplitude of change in the solvent activity.
C	local solvent concentration ($\rho_1/\rho_2 \hat{V}_2$).
D_{12}	binary mutual diffusion coefficient.
D	diffusion coefficient in polymer fixed frame.
D'	coefficient of flow-dependent contribution to the solvent flux.
$\mathcal{D}$	diffusion coefficient for the primitive chain along contour.
$\mathbf{E}^{(2)}$	deformation gradient for polymer component.
f	composition-dependent part of ln a'.
f_{in}	number density of strands with i structural units having junctions of type n.
$f(\mathbf{u},s,t)$	orientation distribution function for primitive chain segments at s.
$g(t)$	time-dependent part of $a(t)$.
G_0	instantaneous modulus of the polymer component.
$G_{0,\mathrm{R}}$	instantaneous modulus of the polymer component according to the reptation model.
$G_{0,\mathrm{T}}$	instantaneous modulus of the polymer component according to the transient network model.
G	coefficient of flow-dependent contribution to ln $a(t)$.
$\mathbf{G}(\mathbf{u})$	rate of change of $\mathbf{u}$ for primitive segments moving affinely with polymer component.

$h(s)$	dimensionless concentration at vapor/liquid interface.
$H(t)$	step function.
$H(\tau)$	shear relaxation spectrum of solution.
H_i	modulus of a strand with i structural units in the limit of small deformations.
$\mathbf{J}_i$	mass flux of i relative to barycentric velocity.
$\mathbf{j}_i$	mass flux of component i in the lab frame.
$\mathbf{j}_1{}^2$	solvent flux in the polymer fixed frame.
k	Boltzmann's constant.
K	constant in the approximation for the Flory–Huggins equation.
K_{ij}	empirical constants in the Vrentas–Duda free volume theory.
k_0	D'/D.
k_1	diffusion Deborah number ($k_1 = \tau D/l^2$).
k_2	dimensionless constant related to the diffusion Deborah number ($k_2 = \tau(D + D')/l^2$).
k_3	$1/k_2$.
l	initial depth of solution.
L	contour length of a primitive chain.
L_{in}	rate of creation of junctions of type n defining strands with i structural units.
M_i	molecular weight of component i.
$M(t)$	mass of solvent in solution.
M_R	memory function for polymer according to the reptation model.
M_T	memory function according to the transient network model.
n_2	molar density of polymer chains.
N	number of primitive segments per chain.
P	thermodynamic pressure.
Q	body heating.
Q_i	partition function for a strand with i structural units.
$\mathbf{q}$	heat flux.
$\mathbf{r}$	position in the lab frame.
$\mathbf{R}$	end-to-end vector for a strand.
R	gas constant.
s	dimensionless time; curvilinear distance along primitive chain.
t	lab time.
t_D	time scale for sorption according to the classical theory.
T	absolute temperature.
$T_g{}^{(2)}$	glass transition temperature of component 2.
$u(x,s)$	dimensionless concentration.
$\mathbf{u}$	unit tangent to the primitive chain at position s.
$\mathbf{v}$	barycentric velocity.
$\mathbf{v}_i$	local average velocity of component i.
$\hat{V}_i$	partial specific volume of i.
$\hat{V}_i{}^*$	specific hard-core volume of i.
V_i	molar volume of i.
$\hat{V}_\mathrm{FH}$	specific hole free volume of solution.
w	dimensionless driving frequency.
$W(s)$	dimensionless mass of solvent in solution.
$W^\mathrm{p}(s)$	steady periodic value of $W(s)$ during oscillatory sorption.
x	dimensionless distance in the polymer fixed frame.
$y^\mathrm{W}(w)$	phase of $W^\mathrm{p}(s)$.
$Y^\mathrm{W}(w)$	amplitude of $W^\mathrm{p}(s)$.
z	distance in the lab frame.

Greek

Γ	change in Helmholtz function relative to pure, undeformed components.
γ	parameter in Vrentas–Duda free volume theory.
$\boldsymbol{\gamma}^{(2)}$	infinitesimal strain tensor for polymer component.
$\boldsymbol{\gamma}'^{(2)}$	infinitesimal displacement gradient for the polymer component.
$\boldsymbol{\delta}$	unit tensor.
¶	entropy.
$\boldsymbol{\eta}$	entropy flux.
η	zero-shear viscosity.
η_l	longitudinal viscosity.
μ_1	solvent chemical potential.
$\mu_1{}^\circ$	solvent standard chemical potential.
ξ	distance in the polymer fixed frame.
Π	isotropic traction experienced by solvent during mutual diffusion.
$\mathbf{\Pi}$	pressure tensor.
ρ	mass density of mixture.
ρ_i	mass density of component i.
σ	entropy production.
τ	shear relaxation time for the polymer component.
τ_i	relaxation times from the transient network model.
τ_l	longitudinal relaxation time for the polymer component.
τ_p	relaxation times from the reptation model.
Φ	change in Gibbs function relative to pure, undeformed components.
ϕ_R	dimensionless relaxation function from the reptation model.
ϕ_T	dimensionless relaxation function from the transient network model.
χ	Flory Huggins interaction parameter.
ω	driving frequency for oscillatory sorption.
ω_i	mass fraction of component i.
Ω	Onsager coefficient.

Accents

ˆ	quantity per unit mass.
ˇ	quantity per unit volume.

Superscripts

(i)	referring to component i.
†	transpose.
−1	inverse.

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Effect of Electrostatic Interaction on the Liquid Crystal Phase Transition in Solutions of Rodlike Polyelectrolytes[†]

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ABSTRACT: It is shown that the effect of electrostatic interactions on the liquid crystal phase transition in solutions of rodlike polyelectrolytes can be characterized by two parameters, one describing the increase of the effective diameter and the other the twisting action. The dependence of these parameters on the charge density and the salt concentration is studied both for weakly charged polyelectrolytes, for which the Debye–Hückel approximation applies, and for highly charged polyelectrolytes, for which the full Poisson–Boltzmann equation has to be used. The isotropic–nematic phase transition cannot be described solely in terms of an effective diameter as has always been done before but one must also take the twisting effect into account. This effect, which enhances the concentrations at the transition, is particularly marked for weakly charged polyions.

I. Introduction

Above a critical concentration solutions of rodlike particles undergo a phase separation into an isotropic phase and an anisotropic phase, coexisting in equilibrium. In the latter phase, which is usually referred to as a lyotropic liquid crystal, the particles have a preferred orientation. This phase separation was first explained by Onsager[1] as the result of the competition between the orientational entropy favoring orientational disorder and the entropy effect associated with the orientation-dependent excluded volume of the rodlike particles which favors orientational order. Onsager calculated explicitly the concentrations of the coexisting phases for the case of monodisperse hard rigid rods. However, many of the particles that form lyotropic liquid crystals are in fact polyelectrolytes, e.g., V_2O_5,[2] γ-AlOOH,[3,4] TMV,[5-9] DNA,[10,11] cellulose microcrystals,[12] Schizophyllan,[13] Scleroglucan,[14] and sickel cell hemoglobin.[15,16] The electrostatic repulsion between the particles influences strongly the formation of the anisotropic liquid crystal phase, as has been particularly well documented for the case of TMV.[6-8] For example, Oster[6] noted that whereas an aqueous solution of TMV freshly purified by ultracentrifugation will separate into isotropic and anisotropic phases if the virus concentration exceeds 2.3%, salts at ionic strengths above 0.005 M cause the system to be fully isotropic. Onsager[1] already indicated that the effect of the electrostatic repulsion will be equivalent to an increase of the effective diameter. This effective diameter will be dependent on the thickness of the electric double layer and thus on the ionic strength. However, the electrostatic repulsion also depends on orientation and thus the effect of the electrostatic repulsion will be different in the isotropic phase from that in the anisotropic phase. Actually the electrostatic interaction favors perpendicular orientation of the particles.

In this paper we take this twisting effect quantitatively into account in the calculation of the isotropic–liquid crystal phase equilibria in solutions of rodlike polyelectrolytes. From our calculations it follows that the importance of the twisting effect is determined by the ratio of the thickness of the electric double layer and the effective diameter of the rods as defined by Onsager.

This paper is organized as follows. In section II we present the relevant theoretical framework that is applied in section III to calculate numerically the concentrations of the coexisting phases. To analyze the results we present in section IV an analytic perturbation treatment of the influence of the twisting effect, and in section V we apply our calculations to some representative systems. The conclusions that can be drawn from this work are collected in section VI.

II. Formalism

We consider a solution of N rodlike polyelectrolytes of length L and diameter D interacting not only electrostatically but also via the hard-core repulsion. There is an excess of 1–1 electrolyte present. The electrostatic interaction between two rods can be written approximately in the form[1,17-19]

$$\frac{w}{k_B T} = \frac{A e^{-\kappa x}}{\sin \phi} \qquad (1)$$

[†] A preliminary version of this paper was reported at the Faraday Discussion on Polymer Liquid Crystals, Cambridge, April 1985.

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