If polymer chains are ruptured to a constant hydrodynamic volume, it is reasonable to assume that they are broken to a shorter average chain length in a good solvent.

They may be highly extended[12] when they receive a shear stress strong enough to break polymer bonds. According to Harrington and Zimm,[12] polymers are considerably extended under a large velocity gradient and under such conditions the Gaussian coil model is no longer possible. On the other hand, the rate constant of scission is considered to be highest near the center of polymer molecules[13-15] under the conditions described in this report, and it is assumed that the shearing forces become smaller away from the center. Such a heterogeneous distribution of shearing forces along polymer chains might affect the shape of the coils. The authors suppose that polymer molecules are deformed to something like the shape of the infinity symbol, "∞", under such shearing forces. Therefore the models shown in Figure 2 ought to be corrected to flat ellipses or stretched shapes under a high velocity gradient. In any event, the authors suspect from the results that, even under a large velocity gradient, the hydrodynamic volume has a certain relation to the scission of a polymer chain in solution by high-speed stirring.

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Diffusion of Polymers Along a Fluid–Fluid Interface

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ABSTRACT: We evaluate the diffusion coefficient for the motion of a polymer along the interface between two fluids. Two polymer models are considered: rigid rods oriented at right angles to the interface, and spherical molecules with their center in the interface.

I. Introduction

The influence of bounding surfaces on the motion of a solid body immersed in a fluid was first investigated by Lorentz[2a] in 1896. He studied the motion of a sphere near a plane wall using a perturbation method, the so-called method of reflections. Subsequently the effect of wall geometry on the motion of more complicated objects has been studied in great detail by the same method.[2b]

In the present article we consider the effect of geometry on the motion of polymers, regarded as diffuse objects rather than as solid bodies. In particular we study the translational diffusion of a polymer adsorbed at the interface between two immiscible fluids. Our primary motivation for studying this problem is the present interest in interfacial phenomena, particularly with regard to the adsorption and mobility of polymeric species at fluid surfaces. The dynamical behavior of macromolecules along interfaces and near walls is of biological interest and potentially may be studied by light scattering and fluorescence spectroscopy. In addition this problem is of theoretical interest because of the present day concern with two-dimensional transport phenomena and the difficulties encountered in the kinetic theory for the transport coefficients. We consider two polymer models, namely, rigid rods oriented perpendicularly to the interface, and diffuse spheres. In a following article we shall investigate the effect of solid walls on the translational diffusion of rigid rod molecules.

We use an approximate expression for the diffusion tensor in terms of the hydrodynamic interaction tensor and the polymer segment distribution, which is a generalization of an expression derived by Kirkwood[3] for diffusion in bulk fluids. The derivation for limited geometry and a discussion of the approximations involved is given in a separate article.

In section II we consider a planar interface between two immiscible fluids and derive the corresponding fundamental solution of the linear Navier–Stokes equations for steady flow. We assume that the surface tension of the interface is so large that it remains planar. In section III we evaluate the translational diffusion coefficient for a rigid rod molecule oriented perpendicularly to the interface. In section IV we consider a spherical polymer and calculate its diffusion coefficient for motion along the interface. Finally, in section V we show that our assumption of large surface tension is an adequate approximation for the situations of interest.

II. Hydrodynamic Interaction Tensor

We consider a polymer immersed in a fluid described by the creeping motion equations, i.e., the Navier–Stokes equation for steady flow with the condition of incompressibility and with neglect of inertial terms.[2] The equations read

$$\eta_0 \nabla^2 \mathbf{V} - \nabla P = \mathbf{F}(\mathbf{r})$$
$$\nabla \cdot \mathbf{V} = 0 \qquad \text{(II.1)}$$

where η_0 is the (local) pure solvent viscosity, $\mathbf{V}(\mathbf{r})$ is the flow velocity, $P(\mathbf{r})$ is the pressure, and $\mathbf{F}(\mathbf{r})$ is the force density exerted on the fluid by the polymer. In the Debye–Bueche picture[4] the force density is given by

$$\mathbf{F}(\mathbf{r}) = \zeta(\mathbf{r})\rho(\mathbf{r})[\mathbf{u}(\mathbf{r}) - \mathbf{V}(\mathbf{r})] \qquad \text{(II.2)}$$

where $\zeta(\mathbf{r})$ is the local friction coefficient, $\rho(\mathbf{r})$ is the polymer segment density, and $\mathbf{u}(\mathbf{r})$ is the rigid body motion of the polymer as a whole. Two of us (B.U.F. and J.M.D.) have shown[5] that eq II.1 and II.2 can be obtained from the microscopic flow equations and the equations describing the hydrodynamic interactions between polymer segments by applying a mean field approximation.

We define the local inverse permeability $\lambda(\mathbf{r})$ of the polymer and the corresponding total inverse permeability Λ by

$$\lambda(\mathbf{r}) = \zeta(\mathbf{r})\rho(\mathbf{r})$$
$$\Lambda = \int \lambda(\mathbf{r})\mathrm{d}\mathbf{r} \qquad \text{(II.3)}$$

Kirkwood's approximate expression[3,6] for the translational diffusion tensor, in a continuum version and as generalized to arbitrary geometry, is given by

$$\mathrm{D} = k_{\mathrm{B}}T\Lambda^{-1}[\mathrm{I} + \Lambda^{-1}\int\int \lambda(\mathbf{r})\mathrm{T}(\mathbf{r},\mathbf{r}')\lambda(\mathbf{r}')\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'] \qquad \text{(II.4)}$$

where $k_{\mathrm{B}}T$ is Boltzmann's constant times absolute temperature, $\mathbf{I}$ is the unit tensor, and $\mathbf{T}(\mathbf{r},\mathbf{r}')$ is the hydrodynamic interaction tensor for the geometry under consideration. $\mathbf{T}$ is found from the fundamental solution of eq II.1 as the velocity response to a point force density $\mathbf{F}(\mathbf{r}) = \mathbf{G}\delta(\mathbf{r} - \mathbf{r}')$,

$$\mathbf{V}(\mathbf{r}) = \mathbf{T}(\mathbf{r},\mathbf{r}') \cdot \mathbf{G} \qquad \text{(II.5)}$$

The corresponding pressure response is given by

$$P(\mathbf{r}) = \mathbf{Q}(\mathbf{r},\mathbf{r}') \cdot \mathbf{G} \qquad \text{(II.6)}$$

In a bulk fluid the Oseen tensor $\mathbf{T}(\mathbf{R})$ and vector $\mathbf{Q}(\mathbf{R})$ depend only on the coordinate difference $\mathbf{R} = \mathbf{r} - \mathbf{r}'$ and are given by

$$\mathrm{T}(\mathrm{R}) = \frac{1}{8\pi\eta_0}\left(\frac{\mathrm{I}}{R} + \frac{\mathrm{RR}}{R^3}\right)$$
$$\mathrm{Q}(\mathrm{R}) = \frac{1}{4\pi}\frac{\mathrm{R}}{R^3} \qquad \text{(II.7)}$$

Our present task is to derive corresponding expressions for the situation of two immiscible fluids separated by a plane interface.

The boundary conditions at the interface are that the velocity $\mathbf{V}(\mathbf{r})$ and the normal-tangential components of the stress tensor must be continuous. The normal-normal component of the stress tensor can have a discontinuity which is balanced by the surface tension and the curvature of the interface. We shall modify these conditions by assuming that the surface tension is so large that the interface remains nearly planar. In the extreme limit of infinite surface tension one has the additional boundary condition that the normal component of $\mathbf{V}$ must vanish at the interface. The normal-normal component of the stress tensor can have a discontinuity from which one can calculate the force exerted on the interface. It will be shown in section V that the approximation of large surface tension is adequate for the situations of interest. Corrections can in principle be calculated. Physically these corrections correspond to distortion of the interface that is induced by the motion of the impurity particle.

We choose a coordinate system with the interface as the xy plane and denote the region $z > 0$ as region 1 and $z < 0$ as region 2. The velocity boundary conditions at $z = 0$ then become

$$V_x^{\,1} = V_x^{\,2}, \quad V_y^{\,1} = V_y^{\,2}, \quad V_z^{\,1} = V_z^{\,2} = 0 \qquad \text{(II.8)}$$

The stress tensor is given by

$$\sigma_{\alpha\beta} = \eta_0\left(\frac{\partial V_\alpha}{\partial x_\beta} + \frac{\partial V_\beta}{\partial x_\alpha}\right) - P\delta_{\alpha\beta} \qquad \text{(II.9)}$$

and using (II.8) one finds that the continuity of σ_{xz} and σ_{yz} at $z = 0$ requires

$$\eta_1\frac{\partial V_x^{\,1}}{\partial z} = \eta_2\frac{\partial V_x^{\,2}}{\partial z}, \quad \eta_1\frac{\partial V_y^{\,1}}{\partial z} = \eta_2\frac{\partial V_y^{\,2}}{\partial z} \qquad \text{(II.10)}$$

It is evident that we have adopted a picture of the interface as a mathematical surface where discontinuous change occurs in certain properties, e.g., the shear viscosity. In fact the interfacial region will be diffuse and a continuous change can be expected in the properties as one passes from one bulk phase to the other. When the impurity object's size is large compared with the thickness of the interfacial region we can expect that our analysis will provide an adequate approximate description.

To solve eq II.1 for a point force density and subject to the boundary conditions II.8 and II.10 is tedious. Fourier transform methods may be tried[7] but lead to a solution of complicated form which is not easily applied. In fact it is easier to write down a solution by inspection using image methods. Let the force $\mathbf{G}$ act at a point $\mathbf{r}' = (x',y',z')$ in region 1. We denote the image point of $\mathbf{r}'$ with respect to the xy plane by $\mathbf{r}'^* = (x',y',-z')$. We split the force $\mathbf{G}$ into a component parallel to the interface, $\mathbf{G}_P = (G_x,G_y,0)$, and one perpendicular to the interface $\mathbf{G}_T = (0,0,G_z)$. Define

$$\eta_+ = {}^1\!/_2(\eta_1 + \eta_2), \quad \eta_- = \eta_1 - \eta_2 \qquad \text{(II.11)}$$

Then one may check that a solution is given by the following expressions

$$\mathbf{V}_i = (\mathbf{I}\nabla^2\phi_i - \nabla\nabla\phi_i) \cdot \mathbf{G}_P + (z'\mathbf{k} \times \mathbf{G}_P) \times \nabla\chi_i + (\mathbf{I}\nabla^2\psi_i - \nabla\nabla\psi_i) \cdot \mathbf{G}_T \qquad \text{(II.12a)}$$

$$P_i = -\eta_i(\mathbf{G}_P \cdot \nabla)\nabla^2\phi_i - \eta_i(\mathbf{G}_T \cdot \nabla)\nabla^2\psi_i \qquad \text{(II.12b)}$$

Where the subscript $i = 1, 2$ denotes that $\mathbf{r}$ is in region 1 or 2, $\mathbf{k}$ is a unit vector in the direction of the positive z axis, and the functions ϕ_i, ψ_i, and χ_i are

$$\phi_1 = \frac{1}{8\pi\eta_+}|\mathbf{r} - \mathbf{r}'| + \frac{1}{8\pi\eta_+}\left(\frac{\eta_-}{2\eta_1}\right)[|\mathbf{r} - \mathbf{r}'^*| - |\mathbf{r} - \mathbf{r}'|] - \frac{1}{8\pi\eta_+}\left(\frac{\eta_2}{\eta_1}\right)\frac{zz'}{|\mathbf{r} - \mathbf{r}'^*|}$$

$$\psi_1 = \frac{1}{8\pi\eta_1}[|\mathbf{r} - \mathbf{r}'| - |\mathbf{r} - \mathbf{r}'^*|] + \frac{1}{8\pi\eta_+}\left(\frac{\eta_2}{\eta_1}\right)\frac{zz'}{|\mathbf{r} - \mathbf{r}'^*|}$$

$$\chi_1 = \frac{1}{4\pi\eta_+}\left(\frac{\eta_2}{\eta_1}\right)\frac{1}{|\mathbf{r} - \mathbf{r}'^*|} \qquad \text{(II.13)}$$

and

$$\phi_2 = \frac{1}{8\pi\eta_+}|\mathbf{r} - \mathbf{r}'| - \frac{1}{8\pi\eta_+}\frac{zz'}{|\mathbf{r} - \mathbf{r}'|}$$

$$\psi_2 = -\frac{1}{8\pi\eta_+}\frac{zz'}{|\mathbf{r} - \mathbf{r}'|}$$

$$\chi_2 = \frac{1}{4\pi\eta_+}\frac{1}{|\mathbf{r} - \mathbf{r}'|} \qquad \text{(II.14)}$$

We note that the interface has an effect even when $\eta_1 = \eta_2$. The solution is most easily visualized by considering separately the cases where $\mathbf{G}_P = 0$ and $\mathbf{G}_T = 0$. An important result of this work is the new general expression obtained for the hydrodynamic interaction that relates the velocity field $\mathbf{V}_i$ induced in a two-phase fluid system by a point force disturbance $\mathbf{G}$. The consequences of the modification to the hydrodynamic interaction caused by the interface are examined here for translational diffusion. However, it is clear that knowledge of the modified hydrodynamic interaction permits the examination of many other dynamical interfacial phenomena on a hydrodynamic basis.

One can obtain the fundamental solution for a half-space $z > 0$ with a hard wall at $z = 0$ with stick or slip boundary conditions by taking the limits $\eta_2 \to \infty$ or $\eta_2 \to 0$, respectively.

III. Translational Diffusion Constant for Rod-like Molecules

We now apply the expression II.4 to calculate the diffusion tensor for a rod-like molecule adsorbed at the interface. We assume that the rod remains perpendicular to the interface, that it is held at a particular depth and that it is constrained to lateral motion along the surface. Clearly one can imagine many mechanisms that would lead to violations of these conditions. Some of these mechanisms can be examined within the framework presented here, but at the expense of much more complex analysis.

For reasons of symmetry $D_{xx} = D_{yy}$, and we calculate D_{xx}. We need consider only the terms with $\mathbf{G}_P$ in (II.12). The explicit expressions for the xx component of the interaction tensor $T_{xx}{}^{ij}(\mathbf{r},\mathbf{r}')$, where the superscripts (i,j) indicate that $\mathbf{r}$ is in region i and $\mathbf{r}'$ in region j, are given by

$$T_{xx}{}^{11}(\mathbf{r},\mathbf{r}') = \frac{1}{8\pi\eta_+}\left[\frac{1}{|\mathbf{r} - \mathbf{r}'|} + \frac{(x - x')^2}{|\mathbf{r} - \mathbf{r}'|^3}\right] + \frac{1}{8\pi\eta_+}\left(\frac{\eta_-}{2\eta_1}\right)\left[\frac{1}{|\mathbf{r} - \mathbf{r}'^*|} + \frac{(x - x'^*)^2}{|\mathbf{r} - \mathbf{r}'^*|^3} - \frac{1}{|\mathbf{r} - \mathbf{r}'|} - \frac{(x - x')^2}{|\mathbf{r} - \mathbf{r}'|^3}\right] - \frac{1}{8\pi\eta_+}\left(\frac{\eta_2}{\eta_1}\right) \times zz'\left[\frac{1}{|\mathbf{r} - \mathbf{r}'^*|^3} - 3\frac{(x - x'^*)^2}{|\mathbf{r} - \mathbf{r}'^*|^5}\right] \qquad \text{(III.1a)}$$

$$T_{xx}{}^{21}(\mathbf{r},\mathbf{r}') = \frac{1}{8\pi\eta_+}\left[\frac{1}{|\mathbf{r} - \mathbf{r}'|} + \frac{(x - x')^2}{|\mathbf{r} - \mathbf{r}'|^3}\right] - \frac{1}{8\pi\eta_+}zz'\left[\frac{1}{|\mathbf{r} - \mathbf{r}'|^3} - 3\frac{(x - x')^2}{|\mathbf{r} - \mathbf{r}'|^5}\right] \qquad \text{(III.1b)}$$

with $\mathbf{r}'^* = (x'^*,y'^*,z'^*) = (x',y',-z')$. The expressions for $T_{xx}{}^{12}$ and $T_{xx}{}^{22}$ follow from (III.1a,b) by interchanging η_1 and η_2.

When evaluating the integral in (II.4) along an infinitesimally thin one-dimensional molecule one encounters a short-distance divergence, though no divergence occurs in three dimensions. In order to compare with Kirkwood's result[2b] for the bulk, we shall evaluate the one-dimensional integral introducing a cutoff b at short distances. Let n_i, b_i, and ζ_i be respectively the number of beads, the bond length and the bead translational friction coefficient in region i. Thus we allow a different but uniform chemical composition in the two regions. The length of the molecule in region i is $L_i = n_i b_i$, and $L = L_1 + L_2$ and $n = n_1 + n_2$ give the total length and the total number of monomer units. From (II.4) and (III.1) we find with $\Lambda_i = n_i\zeta_i$

$$D_{xx} = \frac{k_B T}{(\Lambda_1 + \Lambda_2)}\left\{1 + \frac{1}{4\pi\eta_+(\Lambda_1 + \Lambda_2)}\left[\frac{\Lambda_1{}^2}{L_1} \times \left(\left(\ln n_1 - \frac{9}{8}\right) - \left(\ln n_1 - \frac{5}{4} - \ln 2\right)\frac{\eta_-}{2\eta_1}\right) + \frac{\Lambda_2^2}{L_2}\left(\left(\ln n_2 - \frac{9}{8}\right) + \left(\ln n_2 - \frac{5}{4} - \ln 2\right)\frac{\eta_-}{2\eta_2}\right) + L\frac{\Lambda_1\Lambda_2}{L_1L_2}\left(\frac{L_1L_2}{2L^2} - \frac{L_1}{L}\ln\left(\frac{L_1}{L}\right) - \frac{L_2}{L}\ln\left(\frac{L_2}{L}\right)\right)\right]\right\} \qquad \text{(III.2)}$$

Keeping only the terms which survive for n_1 and n_2 large we find

$$D_{xx} = \frac{k_B T}{4\pi(\Lambda_1 + \Lambda_2)^2}\left[\frac{\Lambda_1{}^2}{\eta_1 L_1}\ln n_1 + \frac{\Lambda_2{}^2}{\eta_2 L_2}\ln n_2\right] \qquad \text{(III.4)}$$

The above results may be compared with the diffusion constant $D_{xx}{}^0$ for the same molecule in a fluid of viscosity η_+ without interface. One finds from eq II.7

$$D_{xx}{}^0 = \frac{k_B T}{(\Lambda_1 + \Lambda_2)}\left\{1 + \frac{1}{4\pi\eta_+(\Lambda_1 + \Lambda_2)}\left[\frac{\Lambda_1{}^2}{L_1} \times (\ln n_1 - 1) + \frac{\Lambda_2{}^2}{L_2}(\ln n_2 - 1) - L\frac{\Lambda_1\Lambda_2}{L_1L_2}\left(\frac{L_1}{L} \times \ln\left(\frac{L_1}{L}\right) + \frac{L_2}{L}\ln\left(\frac{L_2}{L}\right)\right)\right]\right\} \qquad \text{(III.5)}$$

Keeping only the terms which survive for n_1 and n_2 large gives the result

$$D_{xx}{}^0 = \frac{k_B T}{4\pi(\Lambda_1 + \Lambda_2)^2}\left[\frac{\Lambda_1{}^2}{\eta_+ L_1}\ln n_1 + \frac{\Lambda_2{}^2}{\eta_+ L_2}\ln n_2\right] \qquad \text{(III.6)}$$

If we set $n_1 = n_2$, $b_1 = b_2$, $\zeta_1 = \zeta_2$, $\eta_1 = \eta_2$ both (III.2) and (III.5) reduce to

$$D_{xx} = \frac{k_B T}{\Lambda}\left[1 + \frac{\Lambda}{4\pi\eta_0 L}(\ln n - 1)\right] \qquad \text{(III.7)}$$

Using the Einstein relation $D_{xx} = k_B T/f_d{}^{xx}$ and again keeping only the logarithmic term in (III.7) we can therefore write (III.4) as

$$D_{xx} = \frac{k_B T}{(\Lambda_1 + \Lambda_2)^2}\left[\frac{\Lambda_1{}^2}{f_{d,1}{}^{xx}} + \frac{\Lambda_2{}^2}{f_{d,2}{}^{xx}}\right] \qquad \text{(III.8)}$$

where $f_{d,i}{}^{xx}$ is the friction coefficient part i the rod would have in bulk fluid i. This clearly exhibits the influence of the interface. We recall that $\Lambda_i = n_i\zeta_i$ is the free draining limit friction coefficient.

It is easily shown that in the isotropic bulk fluid $D_{zz} = 2D_{xx}$ and hence eq III.7 reduces to Kirkwood's result[2b] for the diffusion constant $D = \frac{1}{3}\mathrm{Tr}\mathbf{D}$ of a rigid rod.

Finally, we take limits in eq III.2 which convert the interface into a hard wall with either stick or slip boundary conditions. These special cases are realized by first taking the limit $n_2 \to 0$, noting that Λ_2 is proportional to n_2, followed by the limit $\eta_2 \to \infty$ for stick or $\eta_2 \to 0$ for slip conditions. Thus we obtain expressions for the diffusion coefficient of a molecule moving parallel to a wall in perpendicular position

$$D_{xx}(\text{stick}) = \frac{k_B T}{\Lambda_1}\left[1 + \frac{\Lambda_1}{4\pi\eta_1 L_1}\left(\ln n_1 - \frac{5}{4} - \ln 2\right)\right] \qquad \text{(III.9)}$$

and

$$D_{xx}(\text{slip}) = \frac{k_B T}{\Lambda_1}\left[1 + \frac{\Lambda_1}{4\pi\eta_1 L_1}(\ln n_1 - 1 + \ln 2)\right] \qquad \text{(III.10)}$$

Hence these diffusion constants are practically independent of the boundary conditions at the wall, and almost equal to the bulk expression given by (III.7).

IV. Spherical Molecules

We also evaluate the diffusion coefficient D_{xx} from (II.4) for a spherical polymer situated so that the interface divides it into two hemispheres. We allow a different chemical composition in each of the two hemispheres, but to perform the hemispherical averages of the interaction tensor **T** analytically it is essential to assume that $\lambda_i = \zeta_i\rho_i$ is constant in each hemisphere. It would be desirable to use a Gaussian density distribution but the integrals must then be done numerically.

In performing the hemispherical averages there are four basic integrals required. These are

$$\int_{z>0}\mathrm{d}\mathbf{r}\int_{z' \gtrless 0}\mathrm{d}\mathbf{r}'\frac{1}{|\mathbf{r}-\mathbf{r}'|} = \frac{8\pi^2}{5}R^5\left[\frac{1}{3} \pm \frac{1}{2}\left(\frac{32}{9\pi} - 1\right)\right] \qquad \text{(IV.1a)}$$

$$\int_{z>0}\mathrm{d}\mathbf{r}\int_{z' \gtrless 0}\mathrm{d}\mathbf{r}'\frac{(x-x')^2}{|\mathbf{r}-\mathbf{r}'|^3} = \frac{8\pi^2}{45}R^5\left[1 \pm \left(\frac{136}{15\pi} - \frac{5}{2}\right)\right] \qquad \text{(IV.1b)}$$

$$\int_{z>0}\mathrm{d}\mathbf{r}\int_{z'<0}\mathrm{d}\mathbf{r}'\frac{zz'}{|\mathbf{r}-\mathbf{r}'|^3} = \frac{8\pi^2}{15}R^5\left[\ln 2 + \frac{16}{9\pi} - \frac{4}{3}\right] \qquad \text{(IV.1c)}$$

$$\int_{z>0}\mathrm{d}\mathbf{r}\int_{z'<0}\mathrm{d}\mathbf{r}'\frac{zz'(x-x')^2}{|\mathbf{r}-\mathbf{r}'|^5} = \frac{8\pi^2}{45}R^5\left[\ln 2 + \frac{568}{225\pi} - \frac{23}{15}\right] \qquad \text{(IV.1d)}$$

where each variable runs over a hemisphere in either region 1 or 2 and R is the radius of the particle. In the Appendix we indicate the general method used for evaluating these integrals.

With the aid of these integrals we may easily evaluate (II.4) for a spherical polymer. Remembering that $\lambda_i = \zeta_i\rho_i$ we define

$$\lambda_+ = \frac{1}{2}(\lambda_1 + \lambda_2)$$
$$\lambda_- = \lambda_1 - \lambda_2 \qquad \text{(IV.2)}$$

The result for the diffusion constant for diffusion along the interface then is

$$D_{xx} = \frac{k_B T}{\Lambda} + \frac{k_B T}{5\pi\eta_+ R}\left[1 + \left(\frac{107}{75\pi} - \frac{2}{5}\right)\left(\frac{\eta_+^2}{\eta_1\eta_2}\right)\left(\frac{\lambda_-}{\lambda_+} - \frac{\eta_-}{\eta_+}\right)^2\right] \qquad \text{(IV.3)}$$

where $\Lambda = (4\pi/3)R^3\lambda_+$. In the limit $\lambda_-, \eta_- \to 0$ we have

$$D_{xx} = \frac{k_B T}{\Lambda} + \frac{k_B T}{5\pi\eta_+ R} \qquad \text{(IV.4)}$$

which is identical with the result as found from the Einstein relation and the friction constant in bulk fluid for a uniform sphere of low segment density.[4,8] As in the case of a rigid rod, eq III.7, in this symmetric case the interface has no effect. Since $(107/75\pi) - (2/5) = 0.054$, the deviations from the value to be expected in a bulk solvent without interface are rather small.

In summary then, our expressions III.2 and IV.3 indicate the extent to which diffusion coefficients for motion along an interface differ from the corresponding diffusion coefficients in a bulk solvent. Geometric considerations are important and it is evident that the largest effects are to be seen for linear molecules oriented at right angles to the interface.

It should be noted that our expressions for the diffusion coefficients have physically reasonable limiting behavior when the viscosity of either phase goes to zero; in this limit ζ_i is proportional to η_i.

The model of the interface used here can be applied to study other frictional properties of a two-phase system, but we will reserve such applications to a later date. In the next section we investigate our assumption of large surface tension in greater detail.

V. Forces on the Interface

We return to the fundamental solution of the linear Navier–Stokes equations for a two-fluid system found in eq II.12–14. It is easy to see that $\Delta\sigma_{zz} = \sigma_{zz}^1 - \sigma_{zz}^2 \neq 0$ at the interface, $z = \Theta$. A calculation gives

$$\Delta\sigma_{zz} = -\frac{3z'^2}{2\pi}\frac{\mathbf{G}\cdot(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^5} \qquad \text{(V.1)}$$

where $\mathbf{r} = (x,y,0)$ is in the interface and the force **G** acts at the point $\mathbf{r}' = (x',y',z')$ in region 1. The effect of $\Delta\sigma_{zz}$ is to tend to depress the interface in front of **G** and to lift it behind **G**. Along a line in the interface perpendicular to **G**, $\Delta\sigma_{zz}$ is zero. Although $\Delta\sigma_z z$ falls off rapidly with increasing $R = |\mathbf{r} - \mathbf{r}'|$, it will diverge at $R = 0$ if $\mathbf{r}'$ approaches the interface. Integrating (V.1) over the interface one finds

$$\int\Delta\sigma_{zz}\mathrm{d}x\mathrm{d}y = G_z \qquad \text{(V.2)}$$

which shows that for infinite surface tension the interface has to support the transverse component of force $\mathbf{G}_T$.

At large distances outside the interface the velocity field due to $\mathbf{G}_T$ falls off as $|\mathbf{V}| \sim R^{-2}$, so that $|\sigma| \sim R^{-3}$ and $|\sigma\cdot\mathrm{d}\mathbf{S}| \sim R^{-1}$. Hence no part of $\mathbf{G}_T$ is transmitted to infinity by the fluid. However, for the velocity field arising from $\mathbf{G}_P$ one has $|\mathbf{V}| \sim R^{-1}$ and $\int\sigma\cdot\mathrm{d}\mathbf{S}$ is finite as $R \to \infty$. Integrating over an infinite hemisphere in region 1 or 2 gives

$$\int\sigma_i\cdot\mathrm{d}\mathbf{S} = -(\eta_i/2\eta_+)\mathbf{G}_P \qquad \text{(V.3)}$$

Thus all of $\mathbf{G}_P$ is transmitted to infinity by the fluid, and each half-space contributes according to its viscosity.

For an interface with finite surface tension the $\Delta\sigma_{zz}$ of eq V.1 would indeed produce some curvature of the interface. However, since $\Delta\sigma_{zz}$ falls off rapidly with increasing $|\mathbf{r} - \mathbf{r}'|$ we expect the curvature to be negligible everywhere unless $|\mathbf{r} - \mathbf{r}'|$ is small. To get an idea of how a molecule might affect the interface consider a rigid-rod molecule oriented at right angles to the interface and moving with center of mass velocity **u** parallel to the interface. Let the molecule lie instantaneously along the z axis. Denote the bond length between beads in region i by b_i. Each bead exerts a frictional force on the fluid. Neglecting hydrodynamic interactions one has $\mathbf{G}_P = \zeta_1\mathbf{u}$ for beads in region 1, where ζ_1 is a friction coefficient. We can write ζ_1 as $\zeta_1 = 6\pi\eta_1 a_1$ introducing an effective spherical radius a_1. Using such a force in (V.1), summing over all beads in region 1, and repeating this for region 2 one finds the result

$$\Delta\sigma_{zz} = -(\mathrm{u}\cdot\mathrm{r})\left\{\frac{3\eta_1 a_1}{b_1}\frac{{L_1}^3}{s^2({L_1}^2 + s^2)^{3/2}} - \frac{3\eta_2 a_2}{b_2}\frac{{L_2}^3}{s^2({L_2}^2 + s^2)^{3/2}}\right\} \quad (\mathrm{V.4})$$

where $s = |\mathbf{r}| = \sqrt{(x^2 + y^2)^{1/2}}$. Thus even for an extended distribution of beads there is a rapid fall-off of $\Delta\sigma_{zz}$ with increasing s and in addition there will be considerable cancellation between the contributions from the segments of the molecule in regions 1 and 2. There is still a divergence at $s = 0$, unless $(\eta_1 a_1/b_1) = (\eta_2 a_2/b_2)$, but at such a close distance to the molecule we cannot expect our approximations to be valid.

At temperature T a molecule of total mass M has Brownian motion velocity u of order $u_{\mathrm{th}} = (3k_{\mathrm{B}}T/M)^{1/2}$. The first term of (V.4) is of order $(3\eta_1 a_1/b_1 s)u_{\mathrm{th}}$ for $s \le L_1$, and of order $(3\eta_1 a_1/b_1 s)(L_1^3/s^3)u_{\mathrm{th}}$ for $s > L_1$. If the two fluids are rather similar, then the cancellations due to the second term of (V.4) would give a resultant which might be only a few percent of the first term by itself. However, let us ignore cancellation and ask that this first term by itself should be compensated by a mean radius of curvature $R(s)$ of the interface at distance s given by

$$(3\eta_1 a_1/b_1 s)u_{\mathrm{th}} \approx \alpha/R(s) \qquad (s \le L_1) \quad (\mathrm{V.5})$$

where α is the surface tension. In order to estimate the numerical value of $R(s)$ we consider a polymer of mass $M = nm$ with $m = 100$ amu at an air–water interface. With a value of α suitable for the air–water interface and η_1 for water we find

$$R(s) \ge \frac{\sqrt{n}}{10}\left(\frac{b_1}{a_1}\right)s \quad (\mathrm{V.6})$$

for $s \le L_1$. For a diffuse polymer we expect $(b_1/a_1) \ge 1$, so that for a large enough molecule we will get a negligible curvature at any fixed s value. The above estimate is crude but conservative and it shows that for molecular diffusion along the interface the approximation of large surface tension and the consequent neglect of curvature of the interface is adequate.

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Appendix

Here we sketch briefly how to evaluate the integral IV.1a. Variations of this method were used for (IV.1b–d). We do the integral for the case where r,r' both range over the same hemisphere in region 1. We have

$$\mathcal{I} = \int_{z\ge 0}\mathrm{d}\mathrm{r}\int_{z'\ge 0}\mathrm{d}\mathrm{r}'\frac{1}{|\mathrm{r}-\mathrm{r}'|} = \int_0^R r^2\mathrm{d}r\int_0^R r'^2\mathrm{d}r' K(r,r') = 2\int_0^R r^2\mathrm{d}r\int_0^r r'^2\mathrm{d}r' K(r,r') \quad (\mathrm{A.1})$$

where we have used the symmetry of

$$K(r,r') = K(r',r) = \int_{z\ge 0}\mathrm{d}\Omega\int_{z'\ge 0}\mathrm{d}\Omega'\frac{1}{|\mathrm{r}-\mathrm{r}'|} \quad (\mathrm{A.2})$$

For $r' \le r$ we have

$$\frac{1}{|\mathrm{r}-\mathrm{r}'|} = \frac{4\pi}{r}\sum_{l=0}^{\infty}\frac{1}{2l+1}\left(\frac{r'}{r}\right)^l\sum_{m=-l}^{+l} Y_{lm}^*(\Omega)Y_{lm}(\Omega') \quad (\mathrm{A.3})$$

Letting $r' = \beta r$, with $0 \le \beta \le 1$, we find

$$\mathcal{I} = 8\pi\int_0^R r^4\mathrm{d}r\int_0^1\beta^2\mathrm{d}\beta\sum_{l=0}^{\infty}\frac{\beta^l}{2l+1}\times\sum_{m=-l}^{+l}\int_{z\ge 0}\mathrm{d}\Omega Y_{lm}^*(\Omega)\int_{z'\ge 0}\mathrm{d}\Omega' Y_{lm}(\Omega') \quad (\mathrm{A.4})$$

Using

$$\int_0^1 P_\nu(x)\mathrm{d}x = \sqrt{\pi}\Big/\left[2\Gamma\left(1-\frac{\nu}{2}\right)\Gamma\left(\frac{3}{2}+\frac{\nu}{2}\right)\right] \quad (\mathrm{A.5})$$

we obtain

$$\int_{z\ge 0}\mathrm{d}\Omega Y_{lm}^*(\Omega) = \delta_{m0}\frac{\pi}{2}\frac{\sqrt{2l+1}}{\Gamma\left(1-\frac{l}{2}\right)\Gamma\left(\frac{3}{2}+\frac{l}{2}\right)} \quad (\mathrm{A.6})$$

so that

$$\mathcal{I} = \frac{8\pi^2R^5}{5}\int_0^1\beta^2\mathrm{d}\beta\frac{\pi}{4}\sum_{l=0}^{\infty}\frac{\beta^l}{\Gamma^2\left(1-\frac{l}{2}\right)\Gamma^2\left(\frac{3}{2}+\frac{l}{2}\right)} \quad (\mathrm{A.7})$$

Apart from $l = 0$, only odd l terms are nonvanishing in (A.7) so that letting $l = 2p + 1$ and using $\Gamma^2(\frac{1}{2} - p)\Gamma^2(\frac{1}{2} + p) = \pi^2\sec^2\pi p$ the series can be summed to give

$$\mathcal{I} = \frac{8\pi^2R^5}{5}\int_0^1\beta\left[\beta - 1 + F\left(-\frac{1}{2},-\frac{1}{2};1;\beta^2\right)\right]\mathrm{d}\beta \quad (\mathrm{A.8})$$

with F the usual hypergeometric function. From the identity

$$F\left(-\frac{1}{2},-\frac{1}{2};1;u\right) = \frac{\mathrm{d}}{\mathrm{d}u}\left(uF\left(-\frac{1}{2},-\frac{1}{2};2;u\right)\right) \quad (\mathrm{A.9})$$

we get

$$\mathcal{I} = \frac{8\pi^2R^5}{5}\left\{\frac{1}{3}+\frac{1}{2}\left[F\left(-\frac{1}{2},-\frac{1}{2};2;1\right)-1\right]\right\} \quad (\mathrm{A.10})$$

which is (IV.1a).

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