

# Coordinate Systems for Modeling the Hydrodynamic Resistance and Diffusion Coefficients of Irregularly Shaped Rigid Macromolecules

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**ABSTRACT:** The analysis of the deterministic motion of a rigid molecule through a quiescent viscous liquid is properly carried out with the origin of coordinates at the center of reaction (CR). In treating the stochastic motions of the diffusion of this same body, however, the center of diffusion (CD) is the appropriate origin. For an irregularly shaped macromolecule, the CR and CD generally do not coincide with one another or with the center of mass (CM). The CR is that point at which the translation-rotation coupling resistance tensor is symmetric and at which the trace of the rotational resistance tensor is a minimum. The CD, defined as that point where the translation-rotation coupling diffusion tensor is symmetric, is the point at which the trace of the translational diffusion tensor is a minimum; the macroscopic translational diffusion coefficient corresponds to the value calculated there. Expressions are given for the transformation of the various tensors from one coordinate system to another. These equations are used to derive formulas for the locations of the CR and CD. One example is treated, a bent rigid rod composed of two arms each of length  $L$ . When the angle between the arms is  $90^\circ$ , the distance between the CR and the CD is  $0.03L$ . The physical basis for the origin dependence of the resistance and diffusion coefficients is discussed, as is the reason that the CM, CR, and CD are generally distinct points.

## I. Introduction

A number of recent studies have been devoted to the numerical<sup>11-12</sup> and analytical<sup>13-20</sup> determination of resistance and diffusion coefficients for oddly shaped rigid and flexible particles. Such investigations are important because they provide a framework for the interpretation of experimental measurements of the transport properties of macromolecules and macromolecular aggregates, so that questions of size, configuration, and flexibility can be answered.

One source of error in many of these studies has been the inappropriate choice of coordinate systems. Although Brenner<sup>21,22</sup> showed that the calculated values of the resistance and diffusion coefficients depend on the coordinate system, his result has been widely ignored. He reported that the correct values, corresponding to those which are observed experimentally, are only obtained if the origin is taken at the hydrodynamic center of reaction (CR), a unique point which is generally distinct from the center of mass (CM). We have recently found an error in Brenner's treatment and discovered that the diffusion coefficients have their macroscopic values at the center of diffusion (CD), a point which does not generally coincide with either the CM or the CR. In this paper, we define the CD, we derive an expression which allows the determination of its location, and we examine the dependence of the various resistance and diffusion coefficients on the location of the coordinate system.

## II. Theory

**A. Resistance Coefficients.** The hydrodynamic resistance tensor was first described by Brenner,<sup>21</sup> and his results are summarized and extended in this section. We follow the more compact notation of Happel and Brenner,<sup>22</sup> we introduce additional simplifications in that notation, and we derive some new results.

If a rigid particle moves through a viscous, incompressible fluid at low Reynolds number, its instantaneous motion is described by specifying  $\mathbf{v}_0$ , the velocity at which a point 0, fixed to the particle, moves with respect to a

coordinate system at rest in the fluid, and  $\omega$ , the angular velocity with which the particle rotates about 0. The force  $\mathbf{f}$  and the torque about 0,  $\mathbf{N}_0$ , are

$$\mathbf{f} = -\mathbf{K} \cdot \mathbf{v}_0 - \mathbf{C}_0^\dagger \cdot \omega \quad (1)$$

$$\mathbf{N}_0 = -\mathbf{C}_0 \cdot \mathbf{v}_0 - \Omega_0 \cdot \omega \quad (2)$$

where  $\mathbf{K}$  is the translational resistance tensor,  $\Omega_0$  is the rotational resistance tensor, and  $\mathbf{C}_0$  and  $\mathbf{C}_0^\dagger$  are the translation-rotation coupling resistance tensor and its transpose. Each of these is a  $3 \times 3$  matrix, and eq 1 and 2 differ slightly from Brenner's expressions<sup>21,22</sup> because we have followed the more conventional form and included the viscosity into the resistance coefficients. The subscript 0 identifies those quantities whose values depend on the location of the origin of coordinates.

These equations can be cast into a more compact form by introducing the generalized velocity  $\mathbf{u}_0$ , a six-vector whose components are those of  $\mathbf{v}_0$  and  $\omega$ , and the generalized force  $\mathbf{F}_0 = (\mathbf{f}, \mathbf{N}_0)$ . Then, gathering the resistance tensors into a single  $6 \times 6$  resistance tensor

$$\mathbf{R}_0 = \begin{pmatrix} \mathbf{K} & \mathbf{C}_0^\dagger \\ \mathbf{C}_0 & \Omega_0 \end{pmatrix} \quad (3)$$

allows the combination of eq 1 and 2 to give

$$\mathbf{F}_0 = -\mathbf{R}_0 \cdot \mathbf{u}_0 \quad (4)$$

This expression is simply the generalized Stokes relationship, with force proportional to velocity. It is a tensor relationship because, in the most general case, the force is not antiparallel to the velocity: the off-diagonal elements of  $\mathbf{K}$  and  $\Omega_0$  reflect this fact for translation and rotation, respectively, while the elements of  $\mathbf{C}_0$  are nonzero if there is hydrodynamic coupling between the translational and rotational motions. If the particle has some symmetry, some of the elements of  $\mathbf{R}_0$  may be zero. The effects of particle symmetry on the resistance coefficients are well described elsewhere,<sup>22</sup> and we will not examine them further here.

To fully characterize these tensors, we need to know how to transform them from one coordinate system to another. First, at a given origin, rotations are described by the ordinary transformation rule

$$\mathbf{A}_0' = \mathbf{\Gamma} \cdot \mathbf{A}_0 \cdot \mathbf{\Gamma}^\dagger \quad (5)$$

where  $\mathbf{A}_0$  and  $\mathbf{A}_0'$  are the  $3 \times 3$  resistance tensor ( $\mathbf{K}$ ,  $\Omega_0$ , or  $\mathbf{C}_0$ ) in the two coordinate systems, and  $\mathbf{\Gamma}$  is the usual orthogonal rotation matrix. Second, if the coordinate system at point P is parallel to that at 0 and if  $\mathbf{r} = (x, y, z)$  is the vector from 0 to P, then

$$\mathbf{K}_P = \mathbf{K}_0 = \mathbf{K} \quad (6)$$

$$\Omega_P = \Omega_0 - \mathbf{U} \cdot \mathbf{K} \cdot \mathbf{U} + \mathbf{C}_0 \cdot \mathbf{U} - \mathbf{U} \cdot \mathbf{C}_0^\dagger \quad (7)$$

$$\mathbf{C}_P = \mathbf{C}_0 - \mathbf{U} \cdot \mathbf{K} \quad (8)$$

where we have introduced the transformation matrix

$$\mathbf{U} = \begin{pmatrix} 0 & -z & y \\ z & 0 & -x \\ -y & x & 0 \end{pmatrix} \quad (9)$$

It is easy to show that the matrix operations  $\mathbf{U} \cdot$  and  $\cdot \mathbf{U}$  are identical with the vector operations  $\mathbf{r} \times$  and  $\times \mathbf{r}$ , respectively, so eq 6–8 are identical with the expressions given by Brenner (footnote 13 of ref 21). Our expressions have the advantage of being simple matrix operations, and they avoid the complications of the dyadic operations of Brenner's equations.

A transformation relationship for  $\mathbf{R}_0$  is obtained by defining the  $6 \times 6$  matrix

$$\mathbf{Q} = \begin{pmatrix} \mathbf{1} & \mathbf{U} \\ \mathbf{0} & \mathbf{1} \end{pmatrix} \quad (10)$$

where  $\mathbf{1}$  and  $\mathbf{0}$  are the  $3 \times 3$  identity and null matrices, respectively. Since  $\mathbf{U}$  is antisymmetric, it can be shown that

$$\mathbf{Q}^\dagger = \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ -\mathbf{U} & \mathbf{1} \end{pmatrix} \quad (11)$$

$$\mathbf{Q}^{-1} = \begin{pmatrix} \mathbf{1} & -\mathbf{U} \\ \mathbf{0} & \mathbf{1} \end{pmatrix} \quad (12)$$

$$(\mathbf{Q}^\dagger)^{-1} = (\mathbf{Q}^{-1})^\dagger = \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{U} & \mathbf{1} \end{pmatrix} \quad (13)$$

These matrices are identical with the four  $\mathcal{R}$  matrices of Brenner's eq 5.21. Combining eq 3 and 6–11, we obtain the transformation relationship for the resistance tensor

$$\mathbf{R}_P = \mathbf{Q}^\dagger \cdot \mathbf{R}_0 \cdot \mathbf{Q} \quad (14)$$

We observe that  $|\mathbf{U}| = 0$  and  $|\mathbf{\Gamma}| = |\mathbf{Q}| = 1$ . Thus, from eq 5–8 and 14, the determinants of the various resistance tensors are all invariants under transformations of the coordinate system, as are the traces of both  $\mathbf{K}$  and  $\mathbf{C}$ .

Let us now briefly examine the symmetry properties of these tensors. Regardless of the location of 0,  $\mathbf{K}$  and  $\Omega_0$  (and consequently  $\mathbf{R}_0$ ) are symmetric, but this is not generally true for  $\mathbf{C}_0$ . On the other hand, every particle, no matter what its shape, does possess a single point, the hydrodynamic center of reaction (CR) at which the coupling tensor is symmetric. This point can be found if  $\mathbf{R}_0$  is known at some point. The coordinates of the CR are most easily given in the coordinate system which coincides with the principal axes of the translational resistance tensor. In that system,  $\mathbf{K}$  is diagonal, and the vector from 0 to the CR has the components<sup>22</sup>

$$x_{\text{CR}} = \frac{C_{32} - C_{23}}{K_{22} + K_{33}} \quad (15)$$

$$y_{\text{CR}} = \frac{C_{13} - C_{31}}{K_{11} + K_{33}} \quad (16)$$

$$z_{\text{CR}} = \frac{C_{21} - C_{12}}{K_{11} + K_{22}} \quad (17)$$

In addition to the foregoing results, we have observed another interesting property of the CR: it is the point at which the trace of the rotational resistance tensor is a minimum. This is demonstrated by comparing the trace at the CR with  $\text{Tr}(\Omega_P)$ , where P is any point other than the CR. Let the vector from the CR to P be  $\mathbf{r} = (x, y, z)$ . If we use the prime to denote values at P, while unprimed values are those at the CR, then, by eq 7

$$\Omega_{11}' = \Omega_{11} - 2yC_{13} + 2zC_{12} + y^2K_{33} + z^2K_{22} \quad (18)$$

$$\Omega_{22}' = \Omega_{22} + 2xC_{23} - 2zC_{21} + x^2K_{33} + z^2K_{11} \quad (19)$$

$$\Omega_{33}' = \Omega_{33} - 2xC_{32} + 2yC_{31} + x^2K_{22} + y^2K_{11} \quad (20)$$

Now the trace of any matrix is invariant under rotations of the coordinate system; further,  $\mathbf{C}_{\text{CR}}$  is symmetric, so  $C_{ij} = C_{ji}$ , and we obtain

$$\text{Tr}(\Omega_P) = \text{Tr}(\Omega_{\text{CR}}) + x^2(K_{22} + K_{33}) + y^2(K_{11} + K_{33}) + z^2(K_{11} + K_{22}) \quad (21)$$

regardless of the orientation of the coordinate system at P. Since the  $K_{ii}$  are all positive definite,<sup>22</sup> then if P is different from the CR

$$\text{Tr}(\Omega_P) > \text{Tr}(\Omega_{\text{CR}})$$

and the trace of the rotational resistance tensor is a minimum at the CR. We also note that since  $\mathbf{K}$  is independent of the location of the origin, it follows that the minimum value of the trace of  $\mathbf{R}_0$  also occurs at the CR.

**B. Diffusion Coefficients.** The generalized Einstein relationship between the  $6 \times 6$  diffusion tensor  $\mathbf{D}_0$  and the resistance tensor for a rigid particle is<sup>21</sup>

$$\mathbf{D}_0 = kT\mathbf{R}_0^{-1} \quad (22)$$

where  $k$  and  $T$  are Boltzmann's constant and the absolute temperature. An alternative derivation of this equation, based on the random walk model of Brownian motion, has also been given.<sup>19</sup> It is useful to separate the translational and rotational motions by partitioning  $\mathbf{D}_0$  into  $3 \times 3$  submatrices. Since no uniform nomenclature yet exists for the various diffusion tensors, we propose the following:

$$\mathbf{D}_0 = \begin{pmatrix} \mathbf{T}_0 & \mathbf{S}_0^\dagger \\ \mathbf{S}_0 & \mathbf{\Theta} \end{pmatrix} \quad (23)$$

$\mathbf{T}_0$  and  $\mathbf{\Theta}$  are the translational and rotational diffusion tensors, respectively,  $\mathbf{S}_0$  is the translation–rotation coupling diffusion tensor, and the subscript again identifies those tensors whose values depend on the location of the origin. We have chosen these symbols because  $T$  clearly identifies translation,  $\Theta$  is in keeping with the use of  $\Omega$  and other Greek letters to indicate rotation (rotational diffusion coefficients are often indicated by  $\Theta$ ), and  $s$  falls between  $r$  (rotation) and  $t$  (translation) (there is a strongly suggestive similarity in the sibilant sounds of  $S$  and  $C$ ).

The physical significance of the diffusion tensor is that it is the constant of proportionality between the gradient of  $\sigma$ , the particle density in the six-dimensional coordinate space, and the diffusive flux  $\mathbf{J}$ . This is expressed by the generalized Fick law<sup>21</sup>

$$\mathbf{J}_0 = -\mathbf{D}_0 \cdot \nabla \sigma_0$$

Alternatively, we recall that the second moment of the

probability distribution function along the coordinate  $q$  is proportional to time<sup>23,24</sup>

$$\langle q^2 \rangle = 2D_q t$$

where  $D_q$  is the diffusion coefficient along  $q$ . The extension of this relationship to the case where there is hydrodynamic coupling between coordinates  $i$  and  $j$  is given by the covariance between the displacements along those coordinates

$$\sigma_{ij}^2 = 2D_{ij}t \quad (24)$$

Once the resistance tensor is known, the various diffusion tensors can be calculated by using eq 22 and 23, inverting  $\mathbf{R}_0$  and partitioning  $\mathbf{D}_0$ , or the  $3 \times 3$  submatrices of  $\mathbf{R}_0$  can be inverted separately. If the latter course is chosen, the diffusion tensors are

$$\mathbf{T}_0 = kT(\mathbf{K} - \mathbf{C}_0^\dagger \cdot \Omega_0^{-1} \cdot \mathbf{C}_0)^{-1} \quad (25)$$

$$\Theta = kT(\Omega_0 - \mathbf{C}_0 \cdot \mathbf{K}^{-1} \cdot \mathbf{C}_0^\dagger)^{-1} \quad (26)$$

$$\mathbf{S}_0 = -kT\Omega_0^{-1} \cdot \mathbf{C}_0 \cdot (\mathbf{K} - \mathbf{C}_0^\dagger \cdot \Omega_0^{-1} \cdot \mathbf{C}_0)^{-1} \quad (27)$$

If there is no coupling at the CR, that point is called the center of hydrodynamic stress.<sup>22</sup> In that case,  $\mathbf{C}_{CR} = 0$ , the CD coincides with the CR, and the translational and rotational motions are independent of one another, with eq 25–27 becoming

$$\mathbf{T}_{CD} = kT\mathbf{K}^{-1}$$

$$\Theta = kT\Omega_{CR}^{-1}$$

$$\mathbf{S}_{CD} = 0$$

The transformation relations for the diffusion tensors are derived by taking the inverse of eq 14 and substituting the resulting expression into eq 22. This gives the diffusion tensor at the point P in the coordinate system which is parallel to that at 0

$$\mathbf{D}_P = \mathbf{Q}^{-1} \cdot \mathbf{D}_0 \cdot (\mathbf{Q}^{-1})^\dagger \quad (28)$$

Substituting eq 12 and 13 into this expression and partitioning  $\mathbf{D}$  according to eq 23, we obtain

$$\mathbf{T}_P = \mathbf{T}_0 - \mathbf{U} \cdot \Theta \cdot \mathbf{U} + \mathbf{S}_0^\dagger \cdot \mathbf{U} - \mathbf{U} \cdot \mathbf{S}_0 \quad (29)$$

$$\Theta_P = \Theta_0 = \Theta \quad (30)$$

$$\mathbf{S}_P = \mathbf{S}_0 + \Theta \cdot \mathbf{U} \quad (31)$$

These expressions are similar to eq 6–8 for the resistance tensors, if we note the reciprocal roles played by translation and rotation in the two cases. While the *translational* resistance tensor is independent of 0, it is the *rotational* diffusion tensor which shows such independence. The reasons for this behavior are discussed in section III-B.

We note that eq 5 can be applied to  $\mathbf{T}_0$ ,  $\Theta$ , and  $\mathbf{S}_0$  to rotate these tensors from one coordinate system to another. Furthermore, eq 28–31 can be used to prove that the determinants of  $\mathbf{D}$  and the other diffusion tensors are all invariants under coordinate system transformations and that  $\text{Tr}(\Theta)$  and  $\text{Tr}(\mathbf{S})$  are also invariants.

By analogy with the discussion in the previous section, it can be shown that  $\mathbf{T}_0$  and  $\Theta$  (and consequently  $\mathbf{D}_0$ ) are symmetric in all coordinate systems, while  $\mathbf{S}_0$  is not generally symmetric. Whatever the shape of the particle, however, there is a unique point, the center of diffusion (CD), at which  $\mathbf{S}_0$  is symmetric. The proof of the existence and the uniqueness of the CD is very similar to that given by Happel and Brenner<sup>22</sup> for the CR, and it need not be repeated here.

In general, the CD does not coincide with the CR. Although Brenner claimed to have proven their coincidence,

his proof contains an error. If we take the inverses of the two equations in footnote 14 of ref 21, for the case where  $|\mathbf{C}_0| \neq 0$  the proof then hinges on the equality

$$\mathbf{K} \cdot \mathbf{C}_{CR}^{-1} \cdot \Omega_{CR} = \Omega_{CR} \cdot \mathbf{C}_{CR}^{-1} \cdot \mathbf{K}$$

a condition which is not generally true, even though all three tensors are symmetric. We will now derive expressions for the coordinates of the CD and show that this point is normally different from the CR.

The CD can be located if the elements of the diffusion tensors are known at some point 0. We first rotate all tensors into the coordinate system defined by the principal axes of  $\Theta$ ; then the procedure is similar to that used to locate the CR. If  $\mathbf{r} = (x, y, z)$  is now the vector from 0 to the CD

$$x_{CD} = \frac{S_{23} - S_{32}}{\Theta_{22} + \Theta_{33}} \quad (32)$$

$$y_{CD} = \frac{S_{31} - S_{13}}{\Theta_{11} + \Theta_{33}} \quad (33)$$

$$z_{CD} = \frac{S_{12} - S_{21}}{\Theta_{11} + \Theta_{22}} \quad (34)$$

These expressions, while similar to those for the CR, eq 15–17, are not identical to them, and the CD is generally distinct from the CR. One case will suffice to demonstrate this, and it will be presented in section III-A.

The translational diffusion coefficient

$$D_t = \frac{1}{3} \text{Tr}(\mathbf{T}_0) \quad (35)$$

is evidently dependent on the location of 0. If we use the prime to denote values at the point P and unprimed values are those at the CD and if  $\mathbf{r} = (x, y, z)$  is the vector from the CD to P, then eq 29 gives, in the coordinate system where  $\Theta$  is diagonal

$$T_{11}' = T_{11} - 2yS_{31} + 2zS_{21} + y^2\Theta_{33} + z^2\Theta_{22}$$

$$T_{22}' = T_{22} + 2xS_{32} - 2zS_{12} + x^2\Theta_{33} + z^2\Theta_{11}$$

$$T_{33}' = T_{33} - 2xS_{23} + 2yS_{13} + x^2\Theta_{22} + y^2\Theta_{11}$$

in analogy with eq 18–20. The symmetry of  $\mathbf{S}_{CD}$  and the positive definiteness of the  $\Theta_{ii}$  can be used to show that, if P is any point other than the CD

$$\text{Tr}(\mathbf{T}_P) > \text{Tr}(\mathbf{T}_{CD})$$

so that, by eq 35, the translational diffusion coefficient has its minimum value when calculated at the CD. Further, the trace of  $\mathbf{D}_0$  is also a minimum at the CD since  $\Theta$  does not depend on the location of 0.

### III. Discussion

**A. How Far Apart Are the CR and CD?** It was during the examination of the transport properties of rigid bent rods, using previously published numerical methods,<sup>3–8</sup> that the difference between the CR and the CD first came to our attention. From those investigations, which have been presented in greater detail elsewhere,<sup>25</sup> it was found that the CD of a bent rod, composed of two rigid straight rods each of length  $L$  and joined at their ends, is closer to the joint than the CR is. Both the CR and the CD lie on the line bisecting the angle between the subunits, for this line is the intersection of the two symmetry planes. For the case where the rod is bent at an angle of  $90^\circ$  and each arm is modeled by 12 collinear spheres of diameter  $L/12$ , the following values were obtained for the distance between the joint and the hydrodynamic centers:

$$y_{CR} = 0.396L$$

$$\gamma_{CD} = 0.368L$$

$$\gamma_{CR}/\gamma_{CD} = 1.075$$

It is instructive to compare these results with those from an analytical expression for the resistance tensor of a bent rod. Such an expression can be obtained from the upper left-hand  $6 \times 6$  submatrix of the  $7 \times 7$  resistance tensor for a hinged rod given previously.<sup>19</sup> If that matrix is inverted, it is easily seen that the resulting coupling diffusion tensor,  $\mathbf{S}_{CR}$ , is not symmetric, indicating that the CR and CD do not coincide. For a rigid bent rod, the distance between the joint and the CR, obtained by eq 16, is

$$\gamma_{CR} = 2Ls/(3 + s^2) \quad (36)$$

where  $s = \sin(\alpha/2)$ . If we apply eq 33 to this same particle, we obtain

$$\gamma_{CD} = 2Ls/(4 - s^2 + s^4) \quad (37)$$

When the bend angle is  $90^\circ$ , eq 36 and 37 give

$$\gamma_{CR} = 0.404L$$

$$\gamma_{CD} = 0.377L$$

$$\gamma_{CR}/\gamma_{CD} = 1.071$$

in good agreement with the numerical results.

If we note that the center of mass of the bent rod is located at

$$\gamma_{CM} = 2^{1/2}L/4 = 0.354L$$

then it is not surprising that the reaction and diffusion centers are closer to the hinge in the numerical determination than in the analytical case. The former treats a relatively fat bent rod (each arm of axial ratio 12), while the latter considers an extremely thin one (infinite axial ratio), and, with lower axial ratios, the hydrodynamic centers would be expected to be closer to the CM.

**B. Origin Dependence of the Tensors.** At first glance, it appears strange that, although  $\mathbf{K}$  does not depend on the choice of origin,  $\mathbf{T}_0$  does (and conversely for  $\Omega_0$  and  $\Theta$ ). These differences have a simple explanation, based on the origin dependence of the physical parameters which are measured to determine them.

In essence, the origin independence of  $\mathbf{K}$  reflects the fact that the net force acting on the particle is independent of the point at which the measurement is made. The torque, on the other hand, does depend on the point about which it is measured. If the force and torque measured at 0 are  $\mathbf{f}$  and  $\mathbf{N}_0$ , then the torque measured at P is<sup>26</sup>

$$\mathbf{N}_P = \mathbf{N}_0 - \mathbf{r} \times \mathbf{f} \quad (38)$$

where  $\mathbf{r}$  is the vector from 0 to P. The origin dependence of the measured torque is the reason that  $\Omega_0$  and  $\mathbf{C}_0$  vary with the location of 0. In fact, the transformation relations for these tensors can be derived from the transformation relations for force, torque, velocity, and angular velocity.<sup>22</sup>

When we examine the elements of  $\mathbf{D}_0$ , the same kinds of considerations apply. The angular velocity of a rigid particle is the same, regardless of the point about which it is measured, so  $\Theta$ , which represents the rate of stochastic angular motions, is independent of origin. By contrast, when the point 0 moves with a linear velocity  $\mathbf{v}_0$  and the particle rotates about 0 with an angular velocity  $\omega$ , then the velocity of the point P is<sup>26</sup>

$$\mathbf{v}_P = \mathbf{v}_0 - \mathbf{r} \times \omega \quad (39)$$

As a consequence, the coefficients which describe the stochastic linear motions,  $\mathbf{T}_0$ , and those which represent the covariances of the linear and angular motions,  $\mathbf{S}_0$ , are

all origin dependent. The purely angular coefficients,  $\Theta$ , do not depend on the location of the coordinate system.

### C. Why Are the CM, CR, and CD Distinct Points?

The CM is taken as the origin of coordinates in problems of rigid-body dynamics when the motion is unconstrained because it is the point at which the rates of change of the linear and angular momenta are equal to the net force and torque acting on the body, in accord with Newton's second law. When considering a particle moving through a fluid at low Reynolds number, we know the motion is dominated by the very large frictional forces, and we are not dealing with an isolated unconstrained body. The net frictional force acts through the CR. As we have shown, the trace of  $\Omega_0$  is a minimum at that point, so the torque is also a minimum when it is measured about that point. If the system is analyzed in any other coordinate system, torques arising from the effects of eq 38 are introduced, and the trace of  $\Omega_0$  is larger there. These torques are similar to the fictitious forces that must be introduced to describe the motions of rigid bodies in rotating coordinate systems, and treating the motion of a particle through a fluid with the origin at the CR eliminates those torques in much the same way that fictitious forces are eliminated in classical mechanics by analyzing the problem in an inertial coordinate system.

So we see that, just as the inertia of an unconstrained rigid body is best treated at the CM, so the frictional effects are properly included by analyzing fluid dynamics problems of single-body motion at the CR. Now, another set of forces, those due to the stochastic battering of the particle by the molecules of the fluid, must be included when we examine diffusion. The CD is the appropriate origin for this class of problem, and it differs from the CR because of those additional forces. The translational diffusion coefficient has its minimum value at the CD; treating the problem at any other point introduces spurious velocities, eq 39, and  $D_t$  is overstated.

### IV. Conclusions

It is to be expected that whenever a particular set of forces or a particular fluid flow pattern acts upon a macromolecule, there will be a unique point at which the problem is properly analyzed, and its location will depend both on the molecular geometry and on the conditions in the fluid. We have demonstrated here that in a fluid treated as a continuum, where only the frictional forces are to be considered, the center of reaction is that point, while if the random forces due to the molecular motion of the fluid are to be included, the center of diffusion is the correct origin. It is shown in another paper<sup>25</sup> that, if the fluid is in shear, the problem should be treated at yet another distinct point, the center of viscosity.

When transport properties of model macromolecules are calculated, the accuracy of the results depends on a number of factors. Regardless of the approach to the problem, some approximations must be introduced to compensate for the absence of analytic solutions to the fluid flow equations, except for a few cases of very high symmetry. The accuracy of the calculations is inevitably limited by those approximations, so it is essential that further errors not be introduced because of lack of rigor in the treatment. Since the rotational resistance coefficients vary quadratically with the position of the origin (eq 18–21), and since  $D_t$  shows a similar variation (discussion following eq 35), the proper choice of coordinate systems is important. The size of the deviations when  $D_t$  is calculated at the CR instead of the CD are discussed in detail elsewhere,<sup>25</sup> but they are as large as 9% for highly asymmetric particles. The results presented here are intended to facilitate the

more rigorous calculation of the transport properties of model macromolecules.

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## Theory of Unsymmetric Polymer-Polymer Interfaces in the Presence of Solvent

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**ABSTRACT:** A theory is presented of the interfacial properties between two immiscible polymers in the presence of a solvent. We use diffusion equations for the probability densities characterizing the polymer configurations, derived on the basis of the mean-field approximation for the intermolecular interactions. We consider systems with a small compressibility and, for specific calculations, we assume the Flory-Huggins form for the free energy. In the limit of infinite molecular weight for the polymers we solve the mean-field equations numerically to obtain the interfacial tension and density profiles for typical values of the interaction parameters. Calculations for the system poly(dimethylsiloxane)-benzene-polystyrene are also carried out.

In recent years there has been considerable interest in the theory of the interfacial properties of heterogeneous polymeric systems. This interest has been motivated to a great extent by the increasingly important role that polymer blends, grafts, and blocks are playing in modern technology. The use of block copolymers in the development of thermoplastic elastomers, hot melt extrudable adhesives, and protective coatings are but some of the important commercial applications currently in use.<sup>1</sup>

Recently Helfand<sup>2-5</sup> has focused on the details of the microdomain structure of block copolymers and has developed a theory, based on mean-field ideas, for predicting domain sizes for various geometries. However, relatively little work has been done to extend the theory of inhomogeneous polymers to include the effects of solvents, which can have a marked influence on the phase separation and physical properties of block copolymer systems.<sup>6</sup> In this paper we present a theory for predicting interfacial properties between two immiscible homopolymers in the presence of a solvent. Our theoretical formulation constitutes an extension of some recent work by Helfand and Sapse<sup>7</sup> on the saturated homopolymer-solvent interface.

In section I we present the theory, based on the mean-field approximation, and discuss the effect of including nonlocal interactions in the free energy. Although our formulation is quite general, we make use of the Flory-Huggins form of the free energy for specific calculations. Section II contains the calculation of the asymptotic (bulk) properties of the polymer-solvent phases away from the interface and leads to a discussion of the equilibrium phase diagrams for the ternary system. Our free energy density contains a term to suppress local fluctuations in the density which would otherwise accompany phase separation, contrary to observation. The determination of this term, in the limit of zero compressibility, is given in section IIB. The numerical method used to solve the mean-field equations is given in section III, along with calculations of the interfacial density profiles and interfacial tensions for typical interaction parameters. Results for the system PDMS/benzene/PS are given in section IV.

## I. Formulation of Theory

**A. Mean-Field Approximation.** We begin by introducing some standard nomenclature for the quantities of