Stochastic models for solution dynamics: The friction and diffusion coefficients
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Stochastic models for solution dynamics: The friction and diffusion coefficients

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Molecular dynamics simulations are reported for a solute immersed in a monatomic solvent; systems modeled represent monatomic and diatomic solute species (whose atoms are larger and heavier than the solvent), with varying force constant and bond length for the diatomic. From these simulations, autocorrelation functions, diffusion coefficients (D), and friction coefficients (η) are determined; for the diatomic, these are found for both the center-of-mass and relative coordinates. These results are used to develop simple models for D and η, including (for the diatomic relative coordinate) their frequency dependence. The models enable D and η to be readily determined from properties such as bulk viscosity, potential parameters, etc. These D and η can be used to interpret and predict picosecond time scale data for solute dynamics using stochastic models (e.g., the Kramers or Langevin equations) at the molecular level; their theoretical basis is such that they should apply to many types of solute moieties (e.g., aromatic rings) as well as to the large atoms used in the simulations.

I. INTRODUCTION

Stochastic theories have been extensively used to describe the dynamics of a solute molecule immersed in a solvent. Such models are both intuitively appealing and computationally convenient, since they encapsulate the complexities of the solvent dynamics as a friction coefficient or memory kernel, and thus lead to an enormous reduction in the number of variables. These stochastic theories include (i) the Langevin equation (LE) approach, or equivalently, a Fokker–Planck equation (or Smoluchowski equation at longer times), particular applications of which include the well-known Kramers solutions for the rate of passage over a barrier; and (ii) the generalized Langevin equation (GLE). The former have met with some considerable success in interpreting, e.g., experiments on conformational dynamics on the picosecond time scale (e.g., Refs. 3–6) and elementary reactions in fluids. On the other hand, many instances have been found where this simple approach appears invalid (e.g., Ref. 8). A number of workers have found that data which were not in accord with simple Stokes–Einstein models of the friction could be fitted with a frequency-dependent friction (e.g., Ref. 9), an approach which is based on the Grote–Hynes solution of the barrier crossing rate for particles whose dynamics are described by a GLE. Indeed, there has been considerable discussion as to the validity of the Stokes–Einstein relationship at the molecular level (see, e.g., Refs. 1 and 11). Nevertheless, a common feature of stochastic theories is that solvent-induced modifications of the solute dynamics are described in terms of a friction coefficient (which may or may not be frequency dependent).

The present article is the first in a series of papers which explore the applicability of stochastic models to solute dynamics. We concentrate on the applicability of a LE or GLE, rather than on any approximate means of solving these equations for given systems. Questions such as solutions of the Kramers equation over a wide range of time scales and solvent viscosities are not addressed here, but rather we consider the more fundamental question of the validity of the LE upon which the Kramers equation is based. In this initial paper, we first present results from a set of molecular dynamics simulations for a system corresponding to one or two iodine atoms in a liquid argon solvent. These “data” are then used to examine various aspects of existing theories for the relationship between the friction coefficient and viscosity, and in particular (1) the validity of the Stokes–Einstein relation and (2) how one may determine the value of the friction coefficient therein (including its frequency dependence) in terms of bulk and microscopic properties of the system under study.

While molecular dynamics (MD) simulations of pure liquids are quite common, few simulations of dilute solutions have been carried out. By far the most work here has been performed on the I2/solvent system12,13 inspired by the wealth of experimental data thereon.14 Some work has also been carried out on the bromine system.15 In the present paper, we report the results of a series of MD simulations of monatomic and diatomic iodine in a Lennard-Jones fluid (liquid Ar). The object of these simulations is to provide data to test the stochastic models of solution dynamics, and to probe the dependence of the friction coefficient on solute properties. We employ model potentials designed to examine effects due to the interatomic force constant and bond length, and thus our conclusions should have quite wide validity. Simulations include a monatomic solute species as well as a diatomic, so that effects due to center-of-mass and relative motions can be separated. Friction coefficients for both the center-of-mass and relative degrees of freedom will be determined. From these data, the dependence of the friction tensor on bond length and on interatomic potential will be discussed in terms of hydrodynamic theory, kinetic theory, and also some macroscopic concepts. While the solute/

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TABLE I. Potential parameters used in the MD simulations.*

<table>
<thead>
<tr>
<th>Lennard-Jones ( V = 4\epsilon [(\sigma/r)^{12} - (\sigma/r)^{6}] )</th>
<th>Solvent–solvent</th>
<th>Solvent–solute</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \epsilon )</td>
<td>102.4</td>
<td>215.6</td>
</tr>
<tr>
<td>( \sigma )</td>
<td>3.418</td>
<td>3.843</td>
</tr>
</tbody>
</table>

Morse (solute–solute: \( V = D_0(1 - \exp[-\beta(r - r_s)^2]) \))

<table>
<thead>
<tr>
<th>Designation</th>
<th>( N )</th>
<th>( F )</th>
<th>( L )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( D_0 )</td>
<td>( 1.49 \times 10^4 )</td>
<td>( 8 \times 10^2 )</td>
<td>( 1.49 \times 10^4 )</td>
</tr>
<tr>
<td>( \beta )</td>
<td>1.859</td>
<td>1.000</td>
<td>1.859</td>
</tr>
<tr>
<td>( r_s )</td>
<td>2.66</td>
<td>2.66</td>
<td>8.00</td>
</tr>
</tbody>
</table>

*Energies in units of amu \( \AA^2 \) ps\(^{-2} \) (1 amu \( \AA^2 \) ps\(^{-2} \) = 0.842 cm\(^{-1} \)), lengths in \( \AA \). Potential designation: \( N \) = "normal" \( I_2 \), \( F \) = "floppy" \( I_2 \), \( L \) = "long" \( I_2 \), as discussed in the text.

The solvent mass ratio considered in this paper is significantly greater than unity, the size difference is not so large, and it is of interest to determine whether a hydrodynamic description of the friction (embodied by the Stokes–Einstein relation) is better justified than it is for a pure liquid.

Some investigations along these lines have been reported hitherto\(^{16,17} \); however, in these cases, only pure liquids were considered. Brooks and Adelman\(^{13} \) carried out limited MD simulations with a diatomic \((\text{denoted } I_2)\) solute, but did not address the questions which are our present concern.

II. SIMULATION TECHNIQUE

Simulations were performed using the technique of Fisher and Watts.\(^{17} \) The simulation involved 108 particles (one or two of which were the solute) interacting by Morse or Lennard-Jones potentials, with periodic boundary conditions. The technique uses a fourth-order Runge–Kutta integration, with the integration time step chosen sufficiently small \((2 \times 10^{-3} \text{ ps})\) to conserve energy to within 0.01% and total momentum to within \(10^{-12}\) of its thermal value. The time step is considerably smaller than is usual in liquid simulations, because of the presence of a stiff bond between two of the particles.

The various potential parameters used are given in Table I. The solvent parameters correspond to those of liquid argon. Trajectories were performed on a system in which the solute parameters were chosen to model (i) monatomic iodine (denoted \( M \)), (ii) "normal" diatomic iodine (denoted \( N \)), (iii) a diatomic molecule the same as \( N \) except that the vibrational frequency was \(~1/8\) that of \( I_2 \) (denoted \( F \), for "floppy"), and (iv) the same as \( N \) except the equilibrium bond length was large enough to allow the passage of a single solvent atom between the solute atoms (denoted \( L \) for long). The \( L \) system should provide information especially pertinent to the secondary recombination of iodine, while the \( N \) and \( F \) systems should do the same for primary recombination.

We also expect the information gained from these diatomic studies to be useful for interpreting data on larger, rigid moieties such as binaphthyl.

The number density of the solvent was chosen to be \(0.022626 \AA^{-3}\) (corresponding to a density of \(\sim 1.5 \text{ g cm}^{-3} \)).

The simulation temperature \( T \) was \(~255\) K \((kT/\epsilon = 1, \text{ where } k \text{ is Boltzmann's constant and } \epsilon \text{ is the solute–solvent well depth})\). This corresponds to a high pressure \((\sim 3 \times 10^5 \text{ kPa})\), determined from the equation\(^{18} \)

\[
P = \rho kT - \frac{1}{3 V_0} \sum_{i<j} r_{ij} \frac{\partial V(r_{ij})}{\partial r_{ij}},
\]

where \( \rho \) is the density, \( V_0 \) the volume of particles contributing to the summation, \( V \) the potential, and \( r_{ij} \) the distance between particles \( i \) and \( j \); pressures were corrected for energy cutoff errors in the usual way.\(^{19} \)

Before considering the results of these simulations, we consider their accuracy. Since we are interested in quantities involving only one or two (solute) atoms in the ensemble, the results will contain more noise than would an equivalent study of a pure solvent. In the studies reported here, between three and five separate simulations were performed for each of the \( N \), \( F \), and \( L \) systems. Errors quoted are the standard deviations calculated from each individual trajectory. As an additional guide to the extent of statistical convergence, results will also be reported from a subset of these trajectories, totaling \(~50\%\) of the total number of integration steps for each system.

III. RESULTS: MONOMATOMIC SOLUTE

Results for monom atomic solute (\( M \)) provide a reference for the behavior of the diatomic solute, as well as providing tests of various models of friction coefficients at a molecular level. Some of the average thermodynamic quantities are presented in Table II. Figure 1 shows the radial distribution functions \( g(r) \) of solvent about (i) solute atom (---) and (ii) solvent atoms (---...). Curves are from \( M \) trajectories.

TABLE II. Thermodynamic properties from simulations. Designations as in Table I, plus \( M \) = monomatomic solute.

<table>
<thead>
<tr>
<th>Designation</th>
<th>( M )</th>
<th>( N )</th>
<th>( F )</th>
<th>( L )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (K)</td>
<td>254.9</td>
<td>253.4</td>
<td>255.5</td>
<td>258.3</td>
</tr>
<tr>
<td>Pressure (10^7 Pa)</td>
<td>30.8</td>
<td>30.3</td>
<td>30.3</td>
<td>32.2</td>
</tr>
<tr>
<td>Mean square velocity ((\text{A}^2 \text{ps}^{-2}))</td>
<td>4.9</td>
<td>2.4</td>
<td>2.7</td>
<td>2.4</td>
</tr>
<tr>
<td>Mean square solute force ((10^{-7} \text{N}))</td>
<td>11.8</td>
<td>11.9</td>
<td>18.1</td>
<td></td>
</tr>
<tr>
<td>Total No. of integration steps</td>
<td>18750</td>
<td>25000</td>
<td>25000</td>
<td>25000</td>
</tr>
</tbody>
</table>

The simulation temperature \( T \) was \(~255\) K \((kT/\epsilon = 1, \text{ where } k \text{ is Boltzmann's constant and } \epsilon \text{ is the solute–solvent well depth})\). This corresponds to a high pressure \((\sim 3 \times 10^5 \text{ kPa})\), determined from the equation\(^{18} \)

\[
P = \rho kT - \frac{1}{3 V_0} \sum_{i<j} r_{ij} \frac{\partial V(r_{ij})}{\partial r_{ij}},
\]

where \( \rho \) is the density, \( V_0 \) the volume of particles contributing to the summation, \( V \) the potential, and \( r_{ij} \) the distance between particles \( i \) and \( j \); pressures were corrected for energy cutoff errors in the usual way.\(^{19} \)

Before considering the results of these simulations, we consider their accuracy. Since we are interested in quantities involving only one or two (solute) atoms in the ensemble, the results will contain more noise than would an equivalent study of a pure solvent. In the studies reported here, between three and five separate simulations were performed for each of the \( N \), \( F \), and \( L \) systems. Errors quoted are the standard deviations calculated from each individual trajectory. As an additional guide to the extent of statistical convergence, results will also be reported from a subset of these trajectories, totaling \(~50\%\) of the total number of integration steps for each system.

FIG. 1. Radial distribution functions \( g(r) \) of solvent about (i) solute atom (---) and (ii) solvent atoms (---...). Curves are from \( M \) trajectories.
functions of solvent with respect to (i) the solute atom and (ii) other solvent atoms [i.e., the usual solvent \( g(r) \)]. The small fluctuations in the former are the result of noise. Normalized velocity autocorrelation functions \( C_{vv}(t) = \langle \mathbf{v}(0) \cdot \mathbf{v}(t) \rangle / \langle \mathbf{v}(0) \cdot \mathbf{v}(0) \rangle \), calculated from two and three of the three separate trajectories used to produce the subsequent results, are given in Fig. 2. The good agreement over the first 0.5 ps suggests convergence over this time interval; beyond 1 ps, noise appears to dominate.

The simulations of Nakanishi et al.\(^{20}\) indicate that increases in the solute/solvent Lennard-Jones interactions relative to those of the solvent/solvent (as holds for our system) should lead to oscillatory behavior in \( C_{vv} \) with a time scale of \( \leq 0.5 \) ps for Ar as solvent. On the other hand, an increase of the solvent mass (as also holds for this system) was shown to suppress such behavior. The absence of such oscillations for less than 1 ps suggests that the increase in mass dominates. The "permanence of motion" (a long, flat, positive tail) reported by these workers is absent in the present system, presumably due to our higher temperature.

Figure 3 shows the mean square displacement as a function of time, again for all and for some of the \( M \) trajectories. Properly converged linear behavior is apparent from \( \sim 0.4 \) to 1.2 ps. Self-diffusion coefficients were determined from the two equivalent expressions:

\[
D = \frac{1}{6} \lim_{t \to \infty} \frac{1}{t} \langle |x(0) - x(t)|^2 \rangle; \\
D = \frac{1}{3} \int_0^\infty dt \langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle. \tag{2}
\]

Numerical evaluation of the second of these expressions requires the assignment of some (large) time beyond which deviations from limiting behavior are assumed negligible. We suggest here that a suitable, and nonarbitrary, choice is the first zero of the force–velocity autocorrelation function \( C_{FV} \). The rationale for this procedure is based on the relation\(^{21}\)

\[
\frac{-d^2C_{VV}}{dt^2} = \frac{dC_{FV}}{dt} = C_{FF} \tag{3}
\]

and, since \( C_{FF}(t = 0) = 0 \) by time reversal, it follows that

\[
\int_0^\infty dt \ C_{FF}(t) = C_{FV}(t = 0) = 0. \tag{4}
\]

Further, if \( C_{FF} \) vanishes identically beyond a given time, so do \( C_{FV} \) and \( C_{VV} \). Hence the first zero of \( C_{FV} \) provides a logically consistent means of choosing the upper limit of integration. In addition, if the correlation functions are noise dominated beyond this time, then one can expect the contributions from longer times to approximate zero.

Using this method for the second of Eqs. (2), the diffusion coefficients calculated for the \( M \) trajectories were found to be 0.278 and 0.295 \( \text{Å}^2 \text{s}^{-1} \), from the mean square displacement and velocity autocorrelation function, respectively. The good agreement suggests that the foregoing provides a reliable means of estimating the maximum time, and will be used in subsequent results. The self-diffusion coefficient of pure solvent was found by the same method to be 0.52 \( \text{Å}^2 \text{s}^{-1} \).

The friction coefficients \( \xi \) is defined by the Einstein relation

\[
\xi = \langle \mathbf{v}(0) \cdot \mathbf{v}(0) \rangle / 3D. \tag{5}
\]

We thus obtain \( \xi = 5.9 \) ps\(^{-1} \) for the solute atom, and \( \xi = 9.7 \) ps\(^{-1} \) for the pure solvent (for the particular simulation conditions chosen here).

Although in the past it was thought that one can use the time integral of the force–force autocorrelation function to find the friction coefficient (including its frequency dependence),\(^{22}\) it has been shown\(^{17}\) that this method cannot be applied consistently. The long-time integral of the force–force autocorrelation function vanishes, and the use of a plateau value gives results that differ significantly from those obtained by direct evaluation.
A. Models for monatomic friction coefficient

We now consider the molecular mechanisms that give rise to friction, for which an excellent review is available. At intermediate densities, the friction is well modeled by the Enskog result

$$\xi_E = \frac{2}{3} \left( \frac{2\mu}{m} \right) \left( \frac{8kT}{\pi \mu} \right)^{1/2} \pi R_p^2 g(R_p) \rho,$$

(6)

where \( m \) is the solute mass, \( \mu \) is the reduced mass of the solute/solvent pair, \( R_p \) is the position of the maximum in the radial distribution function \( g(r) \), and \( \rho \) is the solvent number density. This formula gives \( \xi = 7.1 \) ps \(^{-1} \) for argon and 3.9 ps \(^{-1} \) for the I atom; both values are significantly less than those calculated from the simulations.

Next, we consider the simple Stokes–Einstein formula for the “hydrodynamic” friction coefficient:

$$\xi_H = 6\pi \eta R_p / m,$$

(7)

where \( \eta \) is the solvent viscosity. We first need a value for \( \eta \). This was estimated from the stress autocorrelation function\(^{23,24} \) to be 0.12 \( \pm \) 0.09 cP; however, the stress autocorrelation function from our simulation was noise dominated (as is often the case\(^{25} \)). We therefore adopt the value of \( \eta = 0.22 \) cP obtained by extrapolation of the available experimental data.\(^{26} \) This, from Eq. (7), gives \( \xi = 10.7 \) ps \(^{-1} \) for argon and 4.2 ps \(^{-1} \) for the iodine atom. These values used \( R_p = \sigma_\sigma / 2 \) for argon and \( R_p = 2\sigma_\sigma - \sigma_\rho \) (the combining rule result), where the subscripts \( \sigma \) and \( \rho \) refer to solute and bath (solvent), respectively. While these values of \( \xi \) are in reasonable agreement with those from the simulations, we note that their ratio (which is independent of the value chosen for \( \eta \)) is far too large: 2.6, compared with the value of 1.6 from the simulations. Thus, the simple hydrodynamic model is inapplicable if one makes consistent estimates of the hydrodynamic radius. Indeed, it is well known that while Eq. (7) often gives a reasonable estimate for the friction coefficient, this is only because of a fortuitous cancellation of errors. The Stokes–Einstein relation cannot be applicable at the molecular level, because the flow patterns of the solvent that characterize bulk hydrodynamics cannot be established on the time scale of momentum reversal of a species of atomic dimensions. On the other hand, the ratio of the Enskog frictions is 1.8, which is much closer to unity.

A refinement for the friction coefficient is that used in many molecular theories, such as that of Hynes et al.\(^{11} \) and renormalized kinetic theory,\(^{27} \) where the diffusion coefficient is predicted to be the sum of the Enskog value and a hydrodynamic contribution. The model of Hynes et al.\(^{11} \) based on a modified hydrodynamic boundary condition, leads to

$$\xi^{-1} = \xi_E^{-1} + \xi_H^{-1} R_p / (R_s + R_b),$$

(8)

where \( R_s \) and \( R_b \) are the hydrodynamic radii of the solute particle and solvent bath particles, respectively. Now, it is apparent that Eq. (8) will lead to a value of \( \xi \) that is smaller than that given by Eq. (6): the hydrodynamic modification to Enskog theory will in fact worsen the disagreement with the simulation data. Indeed, Eq. (8) yields \( \xi = 5.3 \) and 2.6 ps \(^{-1} \) for argon and the iodine atom, respectively. As stated, these values are too small, and the ratio (2.0) is too large.

It is informative to examine the reasons for the inapplicability of Eq. (8). Now, for self-diffusion, Eq. (8) is expected to be valid for \( \rho \sigma^3 \lesssim 0.4 \), whereas the simulations given here have \( \rho \sigma^3 \approx 0.9 \). The mechanism responsible for the increase in friction relative to the Enskog value is caging; the momentum reversal evident in \( C_{vv}(t) \) (particularly for the solvent) leads to a decrease in the integral in Eq. (2), thus increasing \( \xi \). This assertion can be checked by comparison with the hard sphere fluid. For \( \rho \sigma^3 \approx 0.9 \), Alder and Wainwright\(^{28} \) showed that the deviation from the Enskog value was a factor of 1.39 for self-diffusion. If this “caging factor” of 1.39 is used to scale the Enskog estimate of 7.1 ps \(^{-1} \) for the solvent, one obtains \( \xi = 9.9 \) ps \(^{-1} \), in excellent accord with the simulation value (9.7 ps \(^{-1} \)). For the case of a heavy test particle of the same size as the solvent particle, Herman and Alder\(^{29} \) showed that this correction factor was reduced to 1.22 for a solute/solvent mass ratio of 4 (for \( \rho \sigma^3 = 0.9 \)). The interpolated factor for iodine/argon is 1.25. When this is used to scale the Enskog friction, one obtains \( \xi = 4.9 \) ps \(^{-1} \), compared with the simulation value of 5.9 ps \(^{-1} \). This agreement is as good as can be expected, because the iodine is larger than the solvent, and the stronger iodine/argon attractive force compared with that for argon/argon enhances the caging effect above that for the equivalent hard-sphere fluid. This modification of Eq. (6) can be expressed as

$$\xi_E = \frac{2}{3} \left( \frac{2\mu}{m} \right) \left( \frac{8kT}{\pi \mu} \right)^{1/2} \pi R_p^2 g(R_p) \rho,$$

(9)

where \( C \) is the caging factor, estimated as described above.

The values of the friction coefficients predicted by the various models are summarized in Table III. The best simple model currently available is the scaled Enskog theory, Eq. (9) (with the scaling obtained using the data of Refs. 28 and 29). It is obvious from the above analysis that there still exists a need to develop a simple model of friction which accurately takes account of caging. While we note that the use of a memory function with additional parameters can provide the flexibility to fit the oscillatory behavior of \( C_{vv} \) caused by caging, the molecular theories,\(^{27} \) which model such viscoelastic behavior lead to expressions similar to Eq. (8) for self-diffusion, and their complexity is such that the solute size and mass dependences are not clear. The incorporation of scaling as in Eq. (9) seems the best currently available method which can be readily applied.

| TABLE III. Friction coefficients \( \xi \) \( (\text{ps}^{-1}) \) of an I atom and of an Ar atom in bulk argon, as deduced from simulation and as obtained from various models as given. |
|------------------|------------------|------------------|
|                  | Ar atom          | I atom           | Ratio |
| Simulation       | 9.7              | 5.9              | 1.6   |
| Enskog, Eq. (6)  | 7.1              | 3.9              | 1.8   |
| Scaled Enskog, Eq. (9) (hard-sphere scaling) | 9.9 | 4.9 | 2.0 |
| Stokes–Einstein, Eq. (7)* | 10.7 | 4.2 | 2.5 |
| Modified Stokes–Einstein, Eq. (8)* | 5.3 | 2.6 | 2.0 |

* \( \eta = 0.22 \) cP.
* Using scaling factor for equal size, different mass, hard spheres (Ref. 29).
IV. RESULTS: DIATOMIC SOLUTE, CENTER-OF-MASS COORDINATE

Figures 4 and 5 show normalized velocity autocorrelation function and displacement for the center-of-mass coordinate for the $N$, $F$, and $L$ systems; as in Fig. 2, progressive averages are presented as a guide to the extent of conversion. The $N$ (normal $I_2$) and $F$ (floppy $I_2$) results are very similar (and similar to the monatomic 1 of Fig. 2), up to $\sim 0.5$ ps, but are quite different from that for $L$ (long $I_2$). The more rapid decay for $L$ suggests that the long bond length (where solvent atoms can fit between the moieties) has a marked effect on the solute dynamics; this is explored at a later point.

In interpreting these trajectory results, it is necessary first to examine the separation of solute center-of-mass and relative coordinates. For nonmonatomic systems, the diffusion and friction coefficients become tensors, $S$ and $D$. If we consider the six-dimensional system comprising the coordinates of the two solute atoms, the Langevin equation (for example) now takes the form $dv_i/dt = -\xi_i + X$, where $v$ is a vector (tensor of the first rank) representing the six diatomic velocity components (in an appropriate basis set), and $X$ is a randomly fluctuating force. For the generalized Langevin equation, the same relation holds if the components of $\xi$ are interpreted as operators of the form $\int_{t'}^t K_\sigma(t-t')$. If we were to take, as a basis set, three Cartesian vectors representing each atom in the solute diatomic, $\xi$ would be given by

$$\xi = \begin{pmatrix} \xi & I \\ T & 0 \end{pmatrix},$$

where $I$ is the $3 \times 3$ unit tensor, $T$ is a $3 \times 3$ symmetric tensor (describing the solvent coupling of the motion of the solute atoms), and $a$ is some function describing how any direct interaction between the solute atoms affects the friction. For example, according to hydrodynamic theory, $30 a = 1$ and $T$
is the Rotne–Prager tensor. On the other hand, for the case of no solvent coupling (as occurs when the bond length becomes infinite), \( a = 1 \) and \( T \) vanishes. It is however usually more convenient to work in center-of-mass and relative coordinates, in which case Eq. (10) becomes

\[
\xi = \left( a \xi^I + T \right) = kT G^{-1}\xi \tag{11}
\]

In other words, for the noninteracting limit, the components of the friction tensor should be simply the monatomic friction coefficient.

We now consider the relation between the diffusion and friction tensors. From the Einstein relationship, one has

\[
D = \langle \mathbf{v}(0) \mathbf{v}(0) \rangle - kT G^{-1} \tag{12}
\]

with the second equality being valid for thermal distributions of the solute velocity; here \( \mathbf{v} \) is a dyad and \( G \) denotes the inverse mass tensor. For a Cartesian basis set on each atom of a homonuclear diatomic, \( G = m^{-1} I \), where \( m \) is the mass of each atom. It is clear from Eq. (12) that, unlike the friction tensor, the center-of-mass and relative components of \( D \) will differ from those in a Cartesian system, since the components of \( G \) are dependent on the basis set. It is convenient to start with the upper \( 3 \times 3 \) part of the diatomic diffusion tensor, defined by

\[
D_m = (kT/2m) \xi^{-1} \tag{13}
\]

where \( \xi_m = a \xi^I + T \) [see Eq. (11)]. For the center-of-mass motion, it is actually only necessary to consider the trace of this quantity, \( D_{cm} = Tr(D_m) \). We note parenthetically that it has been pointed out that Eq. (12) becomes inaccurate in multiparticle systems if \( D \) is a function of bond length, since in this case the underlying equations of motion become nonlinear. However, in the present case, the vibrating atoms vary only slightly (relative to the bond length) about their mean positions, and thus problems arising from the nonlinearities are likely to be insignificant.

The values of \( D_{cm} \) and \( \xi_{cm} \) (the three equal diagonal components of \( \xi_{cm} \)) obtained from the simulations for the \( N, F, \) and \( L \) trajectories from both the means square displacement and the velocity autocorrelation function are listed in Table IV. As stated above, if there were no interactions between the two atoms in the diatomic (as should occur for long bond lengths), \( a = 1 \), and \( T = 0 \), whence \( D_{cm} = D/2 \), where \( D \) is the monatomic diffusion coefficient.

For the \( L \) case, where the two solute atoms are distinct, two methods have been proposed to incorporate solute structure into the center-of-mass diffusion coefficient. The first assumes hydrodynamic interaction.\(^3\)\(^,\)\(^3\)\(^2\) In this case, \( a = 1 \) and \( T \) is related to the Rogne–Prager tensor

\[
T = -\xi_{H} \frac{R_S}{2r} \left[ I + r^{-2} \right] + 2(R/r)^2 \frac{1}{3} \left( 3 I - r^{-2} \right) \tag{14}
\]

Where \( \xi_{H} \) is the hydrodynamic friction of Eq. (7), \( r \) is the vector connecting the center of the atoms, whose radius is \( R_S \) [see Eq. (7)]. Now, for the \( L \) ("long") system, \( r \leq R_S \). It can then be seen, from Eqs. (11), (13), and (14), that this leads to the following approximate result\(^3\)\(^5\) for \( a = 1 \):

\[
D_{cm} \approx D \left[ 1 + \left( \xi_{cm} / \xi_{H} \right) (R_S/r) \right] \tag{15}
\]

Using the appropriate values (see Table I) for \( R_S (3.843 \, \text{Å}) \) and \( r (8 \, \text{Å}) \), and the values of \( D, \xi \), and \( \xi_{H} \) discussed in the previous section for an iodine atom, a value of \( D_{cm} = 0.19 \, \text{Å}^2 \, \text{ps}^{-1} \) is thus obtained. This must be compared with the value of 0.11 \( \text{Å}^2 \, \text{ps}^{-1} \) from the simulations. This disagreement suggests that the hydrodynamic model does not fully describe the system; there is likely to be a modest contribution to \( \xi_{cm} \) from nonhydrodynamic (molecular) interactions at this separation.

The second model for \( D_{cm} \) derives the interactions from kinetic theory.\(^3\)\(^4\),\(^3\)\(^5\) The result may be expressed in a bond-length dependent form for \( T \), with \( a = 1 \). Calculations based on this theory have been carried out on the relative motion of iodine in solvents of varying densities,\(^3\)\(^5\) and these may be compared with the present values for the center-of-mass motion through Eq. (11). The hard sphere calculations of Schell et al.\(^3\)\(^5\) apply to identical solute and solvent particles with \( \rho o^3 = 0.785 \). For I\(_2\) in Ar, one can use \( \sigma = 2R_S \) as an appropriate scaling length for comparison with their calculations at \( r/\sigma = 1.9 \). This value lies near a cusp in their friction coefficient \( \xi_{11} \), associated with the insertion of a solvent atom at \( r/\sigma = 2.0 \). There is a slight increase in \( \xi_{11} \) above the asymptotic limit in this region, in contrast to the hydrodynamic interaction model of Eq. (14), which gives a decrease of \( \sim 25\% \). For the heavier I atom, the hydrodynamic contribution will be larger, and the net result of cancellations of packing and hydrodynamic effects would be that the friction in the vicinity of 8 Å would be closer to the asymptotic limit. This could explain the observations from the simulations for the \( L \) system that the \( D_{cm} \) (0.11 \( \text{Å}^2 \, \text{ps}^{-1} \)) is quite close to the asymptotic limit of 0.14 \( \text{Å}^2 \, \text{ps}^{-1} \) (\( = D/2 \), see previous section).

---

### Table IV. Average quantities from diatomic trajectories.

<table>
<thead>
<tr>
<th>Designation</th>
<th>( N )</th>
<th>( F )</th>
<th>( L )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure in bulk</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solvent</td>
<td>19.7</td>
<td>19.7</td>
<td>20.3</td>
</tr>
<tr>
<td>Total</td>
<td>20.0</td>
<td>20.0</td>
<td>21.1</td>
</tr>
<tr>
<td>Pressure in interaction</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>sphere</td>
<td>38.9</td>
<td>38.9</td>
<td>41.0</td>
</tr>
<tr>
<td>Total duration</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Intramolecular force</td>
<td>705</td>
<td>773</td>
<td>17.6</td>
</tr>
<tr>
<td>Intramolecular potential</td>
<td>57.7</td>
<td>158</td>
<td>172</td>
</tr>
<tr>
<td>Intramolecular distance</td>
<td>2.67</td>
<td>2.45</td>
<td>8.00</td>
</tr>
<tr>
<td>Velocities: center-of-mass ((\times 2))</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \mathbf{v} \mathbf{v} )</td>
<td>4.72</td>
<td>5.41</td>
<td>4.81</td>
</tr>
<tr>
<td>( \mathbf{v} \mathbf{v} )</td>
<td>1.58</td>
<td>1.73</td>
<td>1.55</td>
</tr>
<tr>
<td>( \mathbf{v} \mathbf{v} )</td>
<td>1.45</td>
<td>1.75</td>
<td>1.74</td>
</tr>
<tr>
<td>( \mathbf{v} \mathbf{v} )</td>
<td>1.64</td>
<td>1.93</td>
<td>1.53</td>
</tr>
<tr>
<td>Velocities: relative ((\pm 2))</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \mathbf{v} \mathbf{v} )</td>
<td>4.76</td>
<td>4.49</td>
<td>5.95</td>
</tr>
<tr>
<td>( \mathbf{v} \mathbf{v} )</td>
<td>0.88</td>
<td>1.69</td>
<td>2.73</td>
</tr>
<tr>
<td>( \mathbf{v} \mathbf{v} )</td>
<td>1.99</td>
<td>1.34</td>
<td>1.71</td>
</tr>
<tr>
<td>( \mathbf{v} \mathbf{v} )</td>
<td>1.79</td>
<td>1.46</td>
<td>1.52</td>
</tr>
<tr>
<td>( D_{cm} ) from mean square displacement</td>
<td>0.22</td>
<td>0.23</td>
<td>0.11</td>
</tr>
<tr>
<td>from ( C_v )</td>
<td>0.23</td>
<td>0.22</td>
<td>0.11</td>
</tr>
<tr>
<td>( \xi_{cm} ) from mean square displacement</td>
<td>3.55</td>
<td>4.02</td>
<td>7.00</td>
</tr>
<tr>
<td>from ( C_v )</td>
<td>3.49</td>
<td>4.10</td>
<td>7.03</td>
</tr>
<tr>
<td>( A' / A )</td>
<td>1.44</td>
<td>1.38</td>
<td>( \ldots )</td>
</tr>
</tbody>
</table>

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Rodger, Sceats, and Gilbert: Stochastic models


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Consider next the $N$ ("normal") and $F$ ("floppy") simulations. As shown in Table IV, these give similar values for $D_{\text{cm}}$ and $\xi_{\text{cm}}$; indeed, the values for these two cases are indistinguishable, given the statistical uncertainties in the simulation results. This suggests that any nonlinearities arising from the amplitude of relative motion which could couple to the center-of-mass motion are small, and can be neglected. Now, the values of $\xi_{\text{cm}}$ for the $N$ and $F$ systems (the mean $\xi_{\text{cm}}$ is 3.8 ps$^{-1}$) are significantly less than that for the monatomic (5.9 ps$^{-1}$). Thus the iodine atoms in $I_2$ for these cases (both with a "normal" bond length) cannot be regarded as uncorrelated particles. If the bond length were contracted to zero (a type of "united atom" limit) then the Enskog expression, Eq. (9), would be applicable; $m$ in Eq. (16) would then be twice the mass of a solute atom $(m_1)$ and $\mu = 2m_m b / (m_b + 2m_m)$. The values of $g(R_p)$ and $\tau_1$, $\tau_2$ would be identical to those of a single iodine atom because these factors are independent of mass. Using these values, the united-atom $\xi_H$ is found to be 2.1 ps$^{-1}$. The caging factor for a solute/solvent mass ratio of 6.4 is not known, but extrapolation of the Herman-Alder results$^{29}$ gives an estimate of 1.1 for this quantity. The scaled united atom Enskog estimate of $\xi_H$ is thus 2.3 ps$^{-1}$, compared with the simulation value of ~4 ps$^{-1}$ for the $N$ and $F$ systems. The difference is significant in so far as the same model for monatomic iodine gives a reasonable result.

The most likely reason for the discrepancy is that the $I_2$ molecule is larger than an $I$ atom. The Enskog friction, Eq. (6), scales as the area $4\pi R_p^2$: the area available for collisions with the solvent. This "available" area will be different for a diatomic, and can be estimated as follows.

For a diatomic solute molecule of bond length $r$, there are two sets of degrees of freedom to consider: that lying along the bond and that perpendicular to it. For the bond lengths considered in the $N$ and $F$ trajectories, there is almost total shielding of the inner faces of each atom $(2r/\sigma_0 \approx 0.7)$. Thus, in the radial dimension, the cross sectional area of the solute in contact with the solvent is reduced by a factor of 2. This is important for the relative coordinate, and will be discussed in the following section.

For the center-of-mass motion, the solute may be modeled by two overlapping spheres. Let $R$ be the radius of each sphere and $\theta$ be the contact angle $(2r < R$; see Fig. 6). The ratio of the cross sectional area $A'$ of the overlapping entity to that of a single sphere $A$ is then given by

\[
A' / A = 2 \left[ 1 - (\theta - \cos \theta \sin \theta) / \pi \right].
\]  

(16)

Average values of this ratio for the $N$ and $F$ trajectories are given in Table IV; the average for the two models is 1.4. The $\xi_H$ can then be scaled again by this factor, to account for the increase in area. This gives $\xi_{\text{cm}} = 3.2$ ps$^{-1}$, in acceptable accord with the simulation value of 3.8 ps$^{-1}$. Note that this model estimate for $\xi_{\text{cm}}$ for the diatomic is 15% lower than the simulation value, almost the same amount as is the corresponding estimate for the iodine atom.

In summary, combining Eqs. (9) and (16) gives the following formula for the center-of-mass friction for a homonuclear diatomic:

\[
\xi_{\text{cm}} = \frac{4C}{3} \left( m_b / (m_b + 2m_m) \right) \left( 4kT(m_b + 2m_m) \right)^{1/2}
\]

\[
\times \pi R_p^2 g(R_p) \left( 1 - \theta - \cos \theta \sin \theta \right),
\]

(17)

where $\cos \theta = r / 2R_p$ (where $r$ is the bond length) and $C$ is the caging factor, estimated as described above. Finally, Eq. (17) can be used to estimate $D_{\text{cm}}$ from the formula $D_{\text{cm}} = kT / 2m_b \xi_{\text{cm}}$.

V. RESULTS: DIATOMIC SOLUTE, RELATIVE COORDINATE

A. Friction coefficients and frequencies

Plots of $C_{VV} (t)$ for the radial (relative) coordinate for the $N$, $F$, and $L$ systems are given in Fig. 7. Three differences with the equivalent plot for the center-of-mass coordinate are immediately apparent: (i) the $C_{VV}$ decays much more slowly; (ii) $C_{VV}$ is strongly affected by the vibrational motion of the diatomic, and (iii) changes in vibrational frequency [i.e., the floppy ($F$) vs the normal ($N$) and long diatomic ($L$) curves] strongly affect $C_{VV} (t)$. Indeed, it has long been recognized$^{36}$ that this frequency dependence arises quite naturally from the GLE. It appears that, unlike the center-of-mass motion, the vibrational motion is essentially unaffected by changes in bond length.

The quantity which we wish to obtain from the simulations is the friction coefficient for the relative coordinate $\xi_{\text{rel}}$. The slow decay of the $C_{VV}$, and the many oscillations therein, pose a problem in the evaluation of $\xi_{\text{rel}}$ through Eqs. (2) and (5); any straightforward numerical integration of the $C_{VV} (t)$ of Fig. 7 will lead to large inaccuracies. Indeed, it is clear from Fig. 7 that the $C_{VV} (t)$ have not properly converged for the $N$ and $L$ systems. This problem is overcome if we make a weak, but nevertheless model-dependent assumption: that the $C_{VV}$ obey a GLE with a particular functional form for the kernel. We consider the Brownian model, in which the kernel is a delta function. $C_{VV}$ can then be approximated by that of a system obeying the Langevin equation with a harmonic oscillator potential. Fitting the expression given in the Appendix for this model to the computed $C_{VV} (t)$ yielded the values of $\xi_{\text{rel}}$ given in Table V. For the $N$ and $L$ systems, the resulting curve was very close to that from the simulations, and the use of more complicated functional forms to fit the simulation $C_{VV} (t)$ did not significantly improve the fit. We therefore take these estimates of $\xi_{\text{rel}}$ to be reliable. For the $F$ system, in which the vibrational fre-

FIG. 6. Definitions of $R$, $r$, and $\theta$ for two overlapping spheres.
A frequency is not so well defined, we expect the corresponding value of \( S_{\text{rel}} \) to be less reliable; this is reflected in the errors quoted in Table V.

Table V reveals that there are very large differences between the \( S_{\text{rel}} \) and the \( \omega \) for the monatomic system (5.9 ps\(^{-1}\)). This difference must arise from the internal motion of the solute, and (as stated above) must also depend on the latter's vibrational frequency \( \omega \).

We now have to address the question of the value of \( \omega \). The average vibrational frequency can be evaluated from the simulations, and is quoted in Table V. Also quoted in Table V are the vibrational frequency of the Morse oscillator used in the simulations, and the harmonic approximation thereto. It can be seen that the frequencies of the isolated molecule are significantly different from those in the solvent (particularly for the case of the floppy, or \( F \), system). The origin of these differences is solvent effects, which have been considered by a number of workers. They can be taken into account by a potential of mean force, but the requisite three-body distribution functions would not be available for a particular system without carrying out a simulation. We here discuss an alternative procedure which provides a convenient way to estimate the frequency change from properties of the solvent and solute that are readily accessible.

This solvent effect might be envisaged as resulting in an additional external force on the diatomic solute along the relative coordinate. Figure 8 displays the average force along the relative degree of freedom as a function of bond length for each system obtained from the simulation data. The force is plotted as a function of a reduced solute bond displacement \( r^* = (r - r_0)/r_0 \), where \( r \) is the bond length, \( r_0 \) is its equilibrium value, and \( r_1 \) is the inner classical turning point displacement for a solute oscillator with an energy equal to the average for the particular trajectory. It can be seen that the forces for all three systems are approximately constant within about \( r^* = 1 \) of the average position. It is this approximately constant force to which one can ascribe the change in frequency. Vibrational frequencies for each system in the presence of this average force were found by numerical integration of the appropriate equations of motion, and are listed in Table V. It is clear that the solvent-induced frequency changes observed in the simulations may be accurately ascribed to this average force arising from solvent packing.

B. Model for average solvent force

The frequency changes were shown above to arise from the solvent-induced average force, which we denote \( \langle F_{\text{solv}} \rangle \).

<table>
<thead>
<tr>
<th>Designation</th>
<th>( N )</th>
<th>( F )</th>
<th>( L )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( S_{\text{rel}} ):</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Simulation</td>
<td>0.28 ± 0.03</td>
<td>2.6 ± 0.6</td>
<td>0.26 ± 0.03</td>
</tr>
<tr>
<td>Theory: Eqs. (19) and (20)</td>
<td>0.25</td>
<td>4.8</td>
<td>0.25</td>
</tr>
<tr>
<td>( \omega ):</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>In presence of solvent (from simulations):</td>
<td>6.55</td>
<td>1.19</td>
<td>6.46</td>
</tr>
<tr>
<td>Free oscillator (harmonic):</td>
<td>6.41</td>
<td>0.80</td>
<td>6.41</td>
</tr>
<tr>
<td>Free oscillator (Morse):</td>
<td>6.39</td>
<td>0.68</td>
<td>6.34</td>
</tr>
<tr>
<td>Morse oscillator plus constant force:</td>
<td>6.58</td>
<td>1.24</td>
<td>6.45</td>
</tr>
</tbody>
</table>

TABLE V. Friction coefficients (\( S_{\text{rel}} \)) and frequencies (\( \omega \)) for the relative coordinate from diatomic trajectories. Units are ps\(^{-1}\). Each entry is from a total of four or five trajectories for each system. Designations in Table I. Uncertainties in \( S_{\text{rel}} \) from results of least-squares fitting \( C_{\text{vv}}(t) \) to GLE with differing forms of kernel.
Before going on to find a model for the \( \omega \) dependence of \( \xi_{\text{rel}} \), it is clearly useful to have a simple model for this \( \langle F_{\text{solv}} \rangle \). This is because we aim to produce models for friction coefficients, etc., using quantities that do not require any simulation (such as the solute and solvent potential parameters and bulk properties such as viscosity). We now provide a semiempirical model for \( \langle F_{\text{solv}} \rangle \).

To begin with, we note that the system for which \( \langle F_{\text{solv}} \rangle \) is small is the \( L \) system, which is the only one in which solvent may readily pass between the solute moieties. This suggests that we can assume \( \langle F_{\text{solv}} \rangle = 0 \) for such systems, and need only consider \( \langle F_{\text{solv}} \rangle \) for systems (such as the \( N \) and \( F \) ones here) where solvent passage between the moieties is impeded. Moreover, this also suggests that \( \langle F_{\text{solv}} \rangle \) contains a component arising from solvent pressure \( P \). The radial force exerted by a pressure \( P \) upon two overlapping spheres of radius \( \sigma/2 \) is \( 2\pi(\sigma/2)^2P \). Taking \( \sigma \) as the Lennard-Jones solute–solvent value of Table I, and the pressure \( P \) in each simulation as given in Table IV (see below), gives a value of 890 amu \( \cdot \) ps\(^{-2} \) for this force, compared to the \( \langle F_{\text{solv}} \rangle \) values from the simulations of 705 and 773 amu \( \cdot \) ps\(^{-2} \) for the \( N \) and \( F \) trajectories (see Table IV). The agreement is quite satisfactory; the slight overestimate probably arises because this model does not take into account the pressure-driven repulsion associated with solvent atoms in the T-shaped configuration of an \( L/Ar \) complex. We therefore adopt the following expression for \( \langle F_{\text{solv}} \rangle \):

\[
\langle F_{\text{solv}} \rangle = 2\pi(\sigma_{ab}/2)^2P. \tag{18}
\]

Note that for comparison with the trajectories, we have used the pressure arising from the interaction sphere used in the simulations, as given in Table V. In practice, the internal pressure would be used in Eq. (18).

The foregoing model for estimating \( \langle F_{\text{solv}} \rangle \) can then be used to determine the solvent dependence of the frequency. We now consider how we may determine the frequency dependence of \( \xi_{\text{rel}} \).

### C. Frequency dependence of relative friction coefficient

There is a considerable body of work on finding the frequency dependence of \( \xi \) from quantities such as the force–force autocorrelation function. However, our purpose here is different, viz., to provide a means of estimating this dependence given solute and solvent properties that do not require simulation data.

One suitable formulation has been provided by Sceats et al.\(^{38} \) This uses the force power spectrum generated by solute/solvent collisions for particles interacting by a Morse potential; they show that the friction coefficient is given by

\[
i_{\text{rel}}(\omega) = \xi 8(\pi/3)^{1/2}z^{2/3} \exp[-3z^{2/3} + 4\pi^{-1}(\epsilon/kT)^{1/2}z^{1/3}], \tag{19}
\]

where \( \xi \) is the friction coefficient for the separate atoms of the diatomic solute molecule, \( z = \pi^{2} - 1/2 \omega/b \), \( \epsilon \) is the solute/solvent well depth, \( b = 2(kT/\mu)^{1/2} \) is the collision bandwidth (inverse collision duration), \( \mu \) is the solute atom/solvent atom reduced mass, and \( \beta \) is the exponential factor in the Morse potential. Equation (19) should be valid for high frequency motions (\( \omega > b \)).

In order to compare Eq. (19) with our simulation results, which use a Lennard-Jones rather than a Morse interaction, we need to find a means of approximating the Morse with a Lennard-Jones potential. Since the key quantities are the well depth and hard-core repulsive interactions, we assume that these two are the same for both the Lennard-Jones and Morse potentials; this specifies the Lennard-Jones \( \epsilon \). We then match the slopes of the two potentials at the innermost classical turning point of a trajectory with the average relative energy. This gives

\[
\beta = (12/\sigma)[1/2(1 + q)]^{1/4}(1 + q^{-1}),
\]

\[
q^2 = 1 + (kT/\epsilon). \tag{20}
\]

The \( \xi_{\text{rel}} \) values found from Eqs. (19) and (20) are given in Table V. These are seen to be in excellent agreement with the simulations for the \( L \) and \( N \) systems (both of which are high frequency), and in acceptable agreement with that for the \( F \) system, even though this is at a frequency which is sufficiently low that one would expect the approximations leading to Eq. (19) to become questionable.

While the result for \( \xi_{\text{rel}} \), using Eq. (19) is good, the influence of screening has not been taken into account. Now, at the vibrational frequencies considered for the \( N \) and \( L \) systems, the flow patterns responsible for hydrodynamic interaction cannot be sustained, and Eq. (14) is thus inapplicable. From the discussion of shielding given in Sec. IV, the \( N \) system would be shielded by a factor of 2, whereas shielding should be small for the \( L \) system. Insofar as the values of \( \xi_{\text{rel}} \)
are very similar, the results suggest that shielding is unimportant at high frequencies.

On the other hand, shielding effects are apparent for the low frequency case, the $F$ (floppy) system, with the $\xi_{rel}$ value from the simulation (2.6 ps$^{-1}$) being much less than the unshielded values (4.8 ps$^{-1}$). For completely overlapped spheres, there is almost total shielding of the inner faces, and the cross section of solute in contact with the solvent is reduced by a factor of 2. Applying this shielding factor of 2 to Eq. (19) yields $\xi_{rel} = 2.4$ ps$^{-1}$ for the $F$ system: a slight underestimate. This argument considers only effects on $\xi_{rel}$ of solvent collisions along the line of centers, whereas collisions perpendicular to this must also influence relative motion, although to a lesser extent. The factor $A' / A$ of Eq. (16) would represent the other extreme for the shielding factor; because it gives the total area reduction, rather than that along the line of centers, it must overcompensate for the effects of perpendicular collisions. Using $A' / A = 1.38$ together with the $\xi_{rel}$ from Eqs. (19) and (20) gives $\xi_{rel} = 3.5$ ps$^{-1}$ for the $F$ system: an overestimate, as expected. Further studies are required to determine the reasons why such shielding is apparently not required for the high frequency motions. One possible cause is the cancellation of packing and hydrodynamic effects discussed in Sec. IV.

In summary, the frequency dependence of $\xi_{rel}$ can be calculated using Eq. (19). For high frequency motions, solvent shielding should not be taken into account. For low frequency motions, the $\xi_{rel}$ of Eq. (19) should be reduced by a factor of 2 if the solute moieties are strongly overlapped.

VI. CONCLUSIONS

By carrying out MD simulations for systems with a heavy atom and a heavy diatomic in a solvent, we have obtained diffusion coefficients and friction coefficients for the monatomic solute, and for the center-of-mass and relative coordinates of the diatomic solute; the frequency dependence of the latter was also obtained. We then used these results to develop models which can be readily used to interpret and predict solute dynamics, without the necessity of obtaining simulation data. It was found that the friction coefficient of the monatomic solute could not be accurately represented by any existing model. If the solute/solvent mass ratio was of order unity, the simple Stokes–Einstein relation, Eq. (7), is accurate, but this may be due to cancellation of errors. The recommended expression for any solute/solvent mass ratio is the scaled Enskog expression, Eq. (9), scaled using hard-sphere results as described in Sec. III. The $R_p$ required in Eq. (9) can be approximated with the Lennard-Jones $\sigma$, while $g(R_p)$ can be obtained without recourse to simulation by using the method of Dymond and Alder. These diatomic center-of-mass friction and diffusion coefficients were successfully modeled by modifying the scaled Enskog theory to take into account the area of the solute actually "visible" to the solvent: Eq. (17). The frequency dependence of the friction coefficient for the relative (radial) coordinate of the diatomic was found to be (i) quite different from the zero-frequency value for the monatomic moieties, and (ii) well fitted by a simple expression based on a binary collision model of the solute/solvent force power spectrum: Eqs. (19) and (20); solvent shielding effects can be taken into account as described in Sec. V C. A semiempirical model was developed for systems where solvent cannot freely pass through the solvent moieties, which enabled the solvent-induced frequency shift of the diatomic to be estimated from the pressure of the solvent: Eq. (18); the solvent force so obtained is used to determine the solvent-induced frequency change as described in Sec. V B. No correction is necessary for systems wherein solvent passes readily between the solute moieties.

These models enable diffusion and friction coefficients to be readily determined from properties of the solute and solvent such as bulk viscosity, density, pressure, potential parameters, etc. These $D$ and $\xi$ can in turn be used to interpret and predict short time scale data for solute dynamics using stochastic theories such as the Smoluchowski or Langevin equations; their theoretical basis is such that it is hoped that they may be applicable to the chemical dynamics of more complex types of solutes (e.g., aromatic rings) as well as to the large atoms used in the simulations.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge the cooperation of Professor Bob Watts, who supplied us with his MD program and guided us in its use. We also deeply appreciate thoughtful and helpful comments made by Professor Casey Hynes.

APPENDIX

We summarize here means whereby values for the friction coefficient can be obtained from simulation data by assuming that the system obeys a GLE with two different kernels: a delta function (i.e., the Langevin equation) and an exponential.

1. Langevin equation for harmonic oscillator potential

The solutions here are well known, and the formula for the velocity autocorrelation function is

$$C_{VV} (t) = kT (\gamma t - \alpha \sin (\alpha t)) / (m \Delta),$$

(A1)

where $m$ is the mass, $\alpha = 1/2 (\xi - \Delta)$, $\gamma = 1/2 (\xi + \Delta)$ and $\Delta = (\xi^2 - 4f/m)^{1/2}$, where $f$ is the force constant. Equation (A1) can be used to evaluate $\xi$ by fitting to the $C_{VV} (t)$ found from the simulations. The fitting can be carried out both by a least-squares global fit, and by fitting the first or higher zeros. In addition, other ways of finding $\xi$ are to fit to force or force/velocity autocorrelation functions, in a similar fashion, and, if the force constant is known (modified if necessary by the average solvent force as described in Sec. V), by fitting $\Delta$ to the characteristic frequency of $C_{VV} (t)$.

2. GLE for free diffusion with exponential kernel

Analytic solutions are known for this problem, and the solutions for the velocity autocorrelation function are, for the underdamped case

$$C_{VV} (t) = e^{-\xi t/2} \sin (\nu t + E),$$

(A2)
where \( E = \tan^{-1}(w/\xi) \), \( \nu = 1/2(4\pi^2 - \xi^2)^{1/2} \), and where \( n/2\pi \) is the vibrational frequency of the free oscillator. Fitting the MD \( C_{vv}(t) \) to Eq. (A2) (either globally or to first or latter zeros), or fitting of other correlation functions, again enables \( \xi \) to be obtained in a number of different ways. Either the critically damped or the underdamped case may be obtained in a number of different ways. The critically damped or the underdamped case may be observed, e.g., in Fig. 4.

33. Y. Ikeda, Kobayashi Risaku Kenkyusho Hokoku 6, 44 (1956).