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APPENDIX

The following expressions (A1) through (A6) were obtained from Eq. (12) by direct differentiations with respect to λ's:

$$\lambda_1^2:\quad E^{(200)}-E^{(100)}=\tfrac{1}{2}R_{1e}^2K_{11}, \tag{A1}$$

$$\lambda_1\lambda_2:\quad E^{(110)}+E^{(000)}-E^{(100)}-E^{(010)}=R_{1e}R_{2e}K_{12}, \tag{A2}$$

$$\lambda_1^3:\quad E^{(300)}-E^{(200)}=\tfrac{1}{6}R_{1e}^3K_{111}+R_{1e}K_{11}, \tag{A3}$$

$$\lambda_1\lambda_2^2:\quad E^{(120)}+E^{(010)}-E^{(110)}-E^{(020)}=\tfrac{1}{2}R_{1e}R_{2e}^2K_{122}, \tag{A4}$$

$$\lambda_1^2\lambda_2:\quad E^{(210)}+E^{(100)}-E^{(110)}-E^{(200)}=\tfrac{1}{2}R_{1e}^2R_{2e}K_{112}, \tag{A5}$$

$$\lambda_1\lambda_2\lambda_3:\quad E^{(111)}+E^{(100)}+E^{(010)}+E^{(001)}-E^{(000)}-E^{(110)}-E^{(011)}-E^{(101)}=R_{1e}R_{2e}R_{3e}K_{123}. \tag{A6}$$

Some examples of evaluation of the energies are

$$E^{(100)}=\langle\Psi^{(000)}\mid -T(R_{1e})+\bar{v}_A\mid\Psi^{(000)}\rangle, \tag{A7}$$

$$E^{(200)}=\langle\Psi^{(100)}\mid -T(R_{1e})+\bar{v}_A-E^{(100)}\mid\Psi^{(000)}\rangle, \tag{A8}$$

$$E^{(300)}=\langle\Psi^{(100)}\mid -T(R_{1e})+\bar{v}_A-E^{(100)}\mid\Psi^{(100)}\rangle, \tag{A9}$$

$$E^{(110)}=\langle\Psi^{(010)}\mid -T(R_{1e})+\bar{v}_A\mid\Psi^{(000)}\rangle+\langle\Psi^{(000)}\mid -T(R_{2e})+\bar{v}_B\mid\Psi^{(100)}\rangle, \tag{A10}$$

where the normalization is chosen such that

$$\langle\Psi^{(000)}\mid\Psi^{(100)}\rangle=\langle\Psi^{(000)}\mid\Psi^{(010)}\rangle=\langle\Psi^{(000)}\mid\Psi^{(001)}\rangle=0. \tag{A11}$$

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[1] R. G. Parr and R. White, J. Chem. Phys. **49**, 1059 (1968).
[2] S. Y. Chang, J. Chem. Phys. **56**, 4 (1972).
[3] R. G. Parr and J. E. Brown, J. Chem. Phys. **49**, 4849 (1968).
[4] J. E. Brown and R. G. Parr, J. Chem. Phys. **54**, 3429 (1971).
[5] As one example of the exceptions, the linear triatomic molecule cannot be treated exactly the same way because of the singularity of $(\partial\theta/\partial R)$ at $\theta=\pi$.
[6] (a) P. Phillipson, J. Chem. Phys. **39**, 3010 (1963); C. A. Coulson and A. C. Hurley, *ibid.* **37**, 448 (1962). (b) T. L. Cottrel and S. Paterson, Trans. Faraday Soc. **47**, 233 (1951).
[7] D. P. Chong, J. Phys. Chem. **75**, 1549 (1971).
[8] (a) D. F. Tuan, J. Chem. Phys. **46**, 2435 (1967); (b) **54**, 4631 (1971).

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Hydrodynamic Theory of the Angular Velocity Autocorrelation Function*

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The angular velocity correlation function is computed using a frequency dependent version of Stokes' Law. The drag torque on a sphere rotating nonuniformly about one of its diagonals is used to compute the relaxation of the angular velocity. It is shown that the asymptotic time dependence of this function goes as $t^{-5/2}$. Consequences of this persistence in the orientational relaxation of molecules is discussed.

INTRODUCTION

In recent publications, Ailawadi and Berne[1] have shown that the angular momentum autocorrelation function should have an asymptotic time dependence, $t^{-5/2}$. These studies were based on generalized hydrodynamic equations[2] which include the total angular momentum as a conserved quantity. The long time tail is a direct consequence of the coupling of the molecular angular momentum to the transverse velocity fluctuations (shear modes) in the liquid and is the direct analogue of the long time tail of the linear momentum autocorrelation function.[3]

In an interesting application of hydrodynamics, Zwanzig and Bixon[4] calculated the linear momentum autocorrelation function by generalizing Stokes' law to a sphere in nonuniform motion in a viscoelastic compressible continuum fluid. The boundary conditions used by them are quite general in that their formula applies to the case intermediate between slip and stick boundary conditions, including these two extremes as special cases. The correlation function that they obtain by a judicious choice of parameters is in striking agreement with computer experiments on liquid argon. Moreover, their correlation function goes asymptotically as $t^{-3/2}$, thus giving the observed long time tail. This treatment, when specialized to an incompressible fluid and stick boundary conditions, gives the linear momentum autocorrelation function for a macroscopic sphere (Brownian particle). It shows that the ordinary Brownian motion theory is inapplicable since it neglects inertial terms. Classical Brownian motion theory is based on the Langevin equation with a drag force calculated on the basis of a uniformly moving sphere, thereby leading to an exponentially decaying autocorrelation function. Zwanzig and Bixon's treatment is essentially based on a drag force computed for a sphere moving with a time dependent velocity. This is more realistic since a Brownian sphere does suffer velocity changes due to collisions. It can be concluded that the linear momentum autocorrelation function for a macroscopic sphere has a $t^{-3/2}$ long time tail.[5]

Encouraged by the success of the Zwanzig–Bixon calculation in accounting for the full time dependence of the linear velocity autocorrelation function, including the long time tail, $t^{-3/2}$, we have undertaken a similar calculation of the angular velocity correlation function (AVCF). This we do for several reasons: (a) to confirm our previous prediction of a $t^{-5/2}$ tail on AVCF, (b) to study how the long time persistence effects emerge from the short time relaxation of the AVCF, (c) to study how the orientational correlation functions (usually computed on the basis of the Debye theory of rotational relaxation) are affected by the long time persistence of the angular velocity, and (d) to see if the rotational diffusion coefficient is modified from its Einstein form $(KT/8\pi\eta a^3)$.

THE ANGULAR VELOCITY AUTOCORRELATION FUNCTIONS

A sphere rotating with the time dependent angular velocity

$$\Omega(t)=(2\pi)^{-1}\int_{-\infty}^{+\infty} d\omega\Omega_\omega \exp(-i\omega t)$$

experiences a drag torque[6]

$$N(t)=(2\pi)^{-1}\int_{-\infty}^{+\infty} d\omega N_\omega \exp(-i\omega t),$$

where the frequency components N_ω and Ω_ω are related by

$$N_\omega=-\zeta(\omega)\Omega_\omega, \tag{1}$$

where $\zeta(\omega)$ is a frequency dependent friction constant.

It is necessary to relate the AVCF to $\zeta(\omega)$. This is simply done as follows. The equation of motion for the angular velocity in an external torque $n(t)$ is

$$-i\omega I\Omega_\omega=N_\omega+n_\omega,$$

where the left hand side is the Fourier transform of the total torque, $(I\Omega)$, and the right hand side is the sum of the Fourier transforms of the drag torque $N_\omega[=-\zeta(\omega)\Omega_\omega]$ and the applied torque n_ω. Solving this equation for Ω_ω gives

$$\Omega_\omega=[-i\omega I+\zeta(\omega)]^{-1}n_\omega.$$

From linear response theory[7] it can be shown that the Laplace transform of the AVCF, $\chi(\omega)$, is simply the functional derivative of Ω_ω with respect to n_ω evaluated at $n_\omega=0$:

$$\chi(\omega)=\int_0^\infty dt \exp(i\omega t)\phi(t)=\beta^{-1}\left(\frac{\delta\Omega_\omega}{\delta n_\omega}\right)_{n_\omega=0}.$$

It follows directly from the last two equations that

$$\chi(\omega)=\beta^{-1}[-i\omega I+\zeta(\omega)]^{-1}. \tag{2}$$

To find the AVCF, all that is required is to determine $\zeta(\omega)$ and to Laplace invert $\chi(\omega)$.

HYDRODYNAMIC DETERMINATION OF THE FRICTION CONSTANTS

In standard references on hydrodynamics,[6] the rotational friction constant, ζ, is evaluated in the following way. The Navier–Stokes equation for a viscous imcompressible fluid is solved subject to stick boundary conditions for a uniformly rotating sphere (sphere with constant angular velocity). The resulting velocity field for the fluid is then used to compute the torque exerted by the fluid on the sphere. This torque is linear in the angular velocity and the constant of proportionality is the friction constant,

$$\zeta_0=8\pi\eta a^3, \tag{3}$$

where η is the viscosity of the fluid and a is the radius of the sphere. When this is substituted in Eq. (2), it is found that

$$\chi(\omega)=\beta^{-1}(-i\omega I+\zeta_0)^{-1}, \tag{4a}$$

$$\phi(t)=(\beta I)^{-1}\exp-(I^{-1}\zeta_0 t). \tag{4b}$$

Moreover, it is found by integrating $\phi(t)$ over time that the rotational diffusion constant is

$$D_R=KT/\zeta_0=KT/8\pi\eta a^3,$$

$$D_R=\chi(0). \tag{5}$$

This is the Einstein relation.

This whole theory is based on the assumption that the drag torque computed for a uniformly rotating sphere can be applied to a sphere which, by virtue of molecular collisions, has an angular velocity which varies in time.

It is a fairly straightforward exercise to compute the drag torque on a sphere executing nonuniform rotational motion around one of its diagonals in an incompressible viscous fluid. In fact, Landau and Lifshitz present this as a problem in their book on fluid mechanics.[6] The result is

$$\zeta(\omega)=8\pi\eta a^3 \times(1+\tfrac{2}{3}\{[(1-i)\lambda^3\omega^{3/2}-i\lambda^3\omega]/(1+2\lambda\omega^{1/2}+2\lambda^2\omega)\}),\quad (6)$$

where

$$\lambda=(a^2\rho/2\eta)^{1/2}.$$

We note that $\zeta(\omega)$ reduces at zero frequency to ζ_0, the friction constant in the case of uniform rotations. Substitution of $\zeta(\omega)$ into Eq. (2) leads to a complicated form for $\chi(\omega)$ which is very difficult to Laplace invert analytically. Nevertheless, we can make some statements about the asymptotic time dependence of the AVCF. We note from Eq. (2) that, for small frequencies, $\chi(\omega)$ has the limiting form

$$\chi(\omega)\underset{\omega\to 0}{\longrightarrow}D_R[1+\sqrt{2}\lambda^3 i(i\omega)^{3/2}],\quad (7)$$

which on inversion gives the assymptotic form for AVCF

$$\phi(t)\underset{t\to\infty}{\longrightarrow}-(9/8\pi)^{1/2}D_R\lambda^3 t^{-5/2}.\quad (8)$$

This result confirms our previous studies of long time presistence effects in angular momentum relaxation.[1] It is a direct consequence of hydrodynamics. It can be connected with the penetration depth of the transverse velocity field due to nonuniform rotations of the sphere.

ORIENTATIONAL RELAXATION

The most commonly used model of orientational relaxation is the Debye model. Implicit in this model is the assumption that the angular momentum of the rotor relaxes on a time scale which is very fast compared to the orientational relaxation time. In this event, the molecule suffers frequent angular momentum changes and its orientation changes by a series of very small steps. If $\mathbf{u}(t)$ is a unit vector along a given radius of the sphere, then according to the Debye theory the orientational correlation functions

$$D_l(t)=\langle P_l[\mathbf{u}(0)\cdot\mathbf{u}(t)]\rangle$$

are exponentially decaying functions of the time,

$$D_l(t)=\exp[-l(l+1)D_R t],$$

with $P_l(x)$ the lth order Legendre polynomial, and D_R the rotational diffusion coefficient, $\chi(0)$. The Laplace transform of $D_l(t)$ is, by definition,

$$\chi_l(\omega)\equiv\int_0^\infty dt\,\exp(+i\omega t)D_l(t),\quad (9)$$

which in the Debye model is

$$\chi_l(\omega)=[-i\omega+l(l+1)D_R]^{-1}.\quad (10)$$

The Debye model is based on the assumption of very rapid angular momentum decay. Because of the existence of a long time tail, this assumption is thrown into question. It is of interest to explore the implications of the long time tail with regard to the orientational correlations.

The Debye theory can be generalized by using the frequency dependent rotational diffusion coefficient.

$$D_R(\omega)=\int_0^\infty dt\,\exp(+i\omega t)\phi(t)=\chi(\omega),\quad (11)$$

which reduces to KT/ζ_0 in the limit $\omega\to 0$. The natural generalization of the Debye theory is then

$$\chi_l(\omega)=[-i\omega+l(l+1)\chi(\omega)]^{-1}.\quad (12)$$

Substitution of $\chi(\omega)$ from Eqs. (2) and (6), followed by an asymptotic expansion of the same kind that yielded Eq. (8), leads to the following asymptotic time dependence for the orientation correlation functions:

$$D_l(t)\underset{t\to\infty}{\longrightarrow}\tfrac{3}{4}(2/\pi)^{1/2}[l(l+1)D_R]^{-1}D_R\lambda^3 t^{-5/2}.\quad (13)$$

We predict, therefore, a $t^{-5/2}$ tail on the orientational correlation functions.

A note of caution is required. The generalization of the Debye theory proposed here has not been rigorously derived. Several years ago Harp and Berne[8] noted from their molecular dynamics studies of diatomic liquids that this generalization should work well if noncentral forces between molecules are strong and collisions are frequent (high density). Zwanzig and Nee[9] have used this generalization in the theory of dielectric relaxation with considerable success. We believe that it gives an adequate approximation to the long time behavior of the orientational correlation functions.

NUMERICAL RESULTS

To conclude this discussion, we make numerical comparisons of results obtained from the hydrodynamic theory and results obtained from the classical Langevin theory. In Fig. 1 we plot the normalized power spectrum of the AVCF, $\chi'(\omega)/\chi'(0)$, where $\chi'(\omega)$ is the real part of the susceptibility $\chi(\omega)$, in reduced units

$$x=\lambda^2\omega,\qquad \lambda^2=a^2\rho/2\eta,$$

for the conditions: temperature T is 273°K, density is 1 g/cc, shear viscosity is 0.01 p, sphere radius is 10^{-4} cm, sphere moment of inertia is 4.20×10^{-20} g·cm^2.

We note from the figure that for these parameters there is a real difference between the hydrodynamic and the classical theories. This difference becomes more important the smaller the quantity,

$$\tilde{I}=I/\lambda^2\zeta_0\simeq\tfrac{1}{3}(\rho_s/\rho),$$

which only depends on the ratio of the sphere's density, ρ_s, to the solvent density, ρ. In this case $\tilde{I}=$

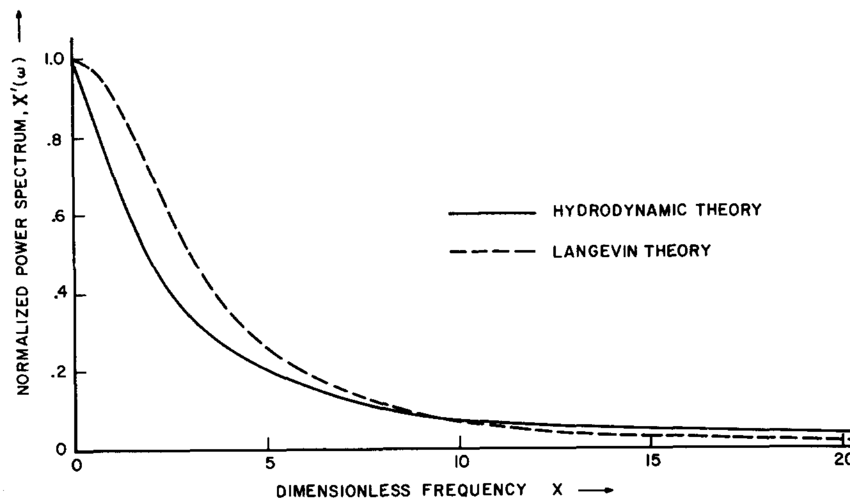

FIG. 1. The normalized spectrum of the angular velocity versus the dimensionless frequency $x=\lambda^2\omega$ for $\tilde{I}=0.333$. The hydrodynamic theory is the solid line (—) and the Langevin theory is the dashed line (---).

0.333. To demonstrate this assertion, we present in Fig. 2 the normalized power spectrum for identical conditions except for a less dense sphere with $\tilde{I}=(4\pi)^{-1}$. This dependence on the ratio (ρ_s/ρ) is probably due to the fact that a more massive sphere would be less affected by the vortex fields it produces than a less massive sphere. This is a kind of fly wheel effect.

Thus we see that the inertial terms in the drag torque on a nonuniformly rotating sphere can have dramatic effects on the AVCF. Let us now investigate whether these dramatic effects would influence the orientational correlation functions and their associated transform, $\chi_l(\omega)$,

$$\chi_l(\omega)=\beta^{-1}[-i\omega+l(l+1)\chi(\omega)]^{-1}.$$

Because

$$l(l+1)\chi(\omega)\leq l(l+1)D_R,$$

the major frequency dependence of $\chi_l(\omega)$ comes from the region

$$\omega\sim l(l+1)D_R.$$

Now if this characteristic frequency is substituted into $\chi(\omega)$, it is found that $\chi(\omega)$ hardly changes from its zero frequency value of D_R, so that

$$\chi_l(\omega)\simeq\beta^{-1}[-i\omega+l(l+1)D_R]^{-1}.$$

This is simply the Debye result. Only for frequencies very much larger than $l(l+1)D_R$ are there any effects to be associated with the hydrodynamic theory. But for such large frequencies, $\chi_l(\omega)\to 0$, and the effects will not be seen. The reason for this is that orientations relax on a time scale $\tau_0=D^{-1}_R$ which is much slower than the time scale $\tau_\Omega=I/\zeta_0$ on which the angular velocity decays:

$$\tau_0/\tau_\Omega=\zeta_0^2/IKT=80\pi\eta^2a/\rho_sKT.$$

For the calculations already presented, this ratio is of order 10^7. It follows that the characteristic frequencies of $\chi_l(\omega)$ and $\chi(\omega)$ are sufficiently different, in the ratio 10^{-7}, that the Debye theory of orientational relaxation is quite adequate. In order to observe deviations from the Debye theory of orienta-

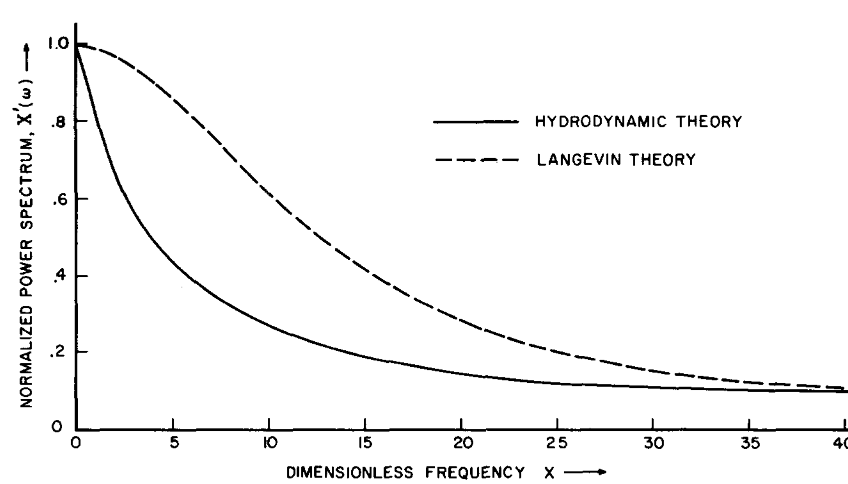

FIG. 2. The normalized spectrum of the angular velocity versus the dimensionless frequency $x=\lambda^2\omega$ for $\tilde{I}=1/4\pi$. The hydrodynamic theory is the solid line (—) and the Langevin theory is the dashed line (---).

tion it would be necessary to go out into the wings of $\chi_l(\omega)$. This is not experimentally feasible. We see that the ratio ζ_0^2/IKT is most critically dependent on the radius a. The question immediately arises: Is there any possibility of studying spheres sufficiently small that the time scales for reorientation, and angular velocity relaxation are not so well separated? The radius that would be required would then be

$$a \simeq \rho_s KT/80\pi\eta^2 \simeq 10^{-12},$$

which is clearly absurd. We conclude that the long time effects would not be likely to show up in studies of the orientational correlation functions, and are forced to look for them in the AVCF using either molecular dynamics or spin rotation coupling magnetic relaxation. We are presently trying to extend this treatment to a viscoelastic treatment of the AVCF.

DISCUSSION

It should be noted that, in an incompressible fluid, the motion of a macromolecule is accompanied by an instantaneous displacement of the fluid, whereas in a real compressible fluid, there is a time lag between the displacement of the macromolecule and the motion of the fluid. This has some very important consequences. In an incompressible fluid:

(a) the initial value of the linear velocity autocorrelation function is

$$\langle V_x^2 \rangle = KT/M^*,$$

(b) the initial value of the AVCF is

$$\langle \Omega^2 \rangle = KT/I^*,$$

(c) the translational and rotational diffusion constants are given by their Stokes' law values, $KT/6\pi\eta a$ and $KT/8\pi\eta a^3$, respectively, even when the drag force and torque are correctly computed as in this paper.

Here M^* and I^* are the effective mass and moment of inertia.

Statistical mechanics, of course, requires that the mass and moment of inertia rather than the effective mass and the effective moment of inertia appear in $\langle V_x^2 \rangle$ and $\langle \Omega^2 \rangle$. Thus, the incompressible fluid calculation is far from correct at short times. When the calculation is done for a compressible fluid, the correct result is obtained; but then the diffusion coefficients contain a small correction to their Stokes' law values. This latter point was not noted by Widom in his treatment of translational Brownian motion.

In conclusion, we would like to point out that Gordon and Messenger[10] have some preliminary results on long cylinders rotating about the cylindrical axis. Although they do not calculate the AVCF, they do calculate how a given initial angular velocity decays to zero. They find for this case that there is a long time tail of t^{-1}. This is a much longer tail than we have found, and seems to indicate that geometrical shape can be exceedingly important. Nevertheless, it should be born in mind that, with regard to translational motion, the cylinder acts very peculiarly in that even in uniform motion it does not obey Stokes' law; that is, the drag force is nonlinear in the velocity. Perhaps the Gordon–Messenger result reflects analogous behavior in the rotational motion. In order to study the effects of molecular geometry we have performed a calculation, of the AVCF of a disk rotating about an axis perpendicular to its plane, and find that in this case the long time tail is also $t^{-5/2}$.

SUMMARY

The AVCF for a sphere rotating in a viscous incompressible fluid has a persistence of velocity which gives rise to an asymptotic $t^{-5/2}$ tail. This tail results from a purely hydrodynamic interaction between the sphere and its host fluid.

In ordinary fluids, it is not expected that this persistence could easily be observed in the long time behavior of the orientational correlation functions, despite the fact that these functions should in principle go as $t^{-5/2}$.

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[1] N. K. Ailawadi and B. J. Berne, J. Chem. Phys. **54**, 3569 (1970); IUPAP Conference on Statistical Physics, Chicago, March, 1971.

[2] N. K. Ailawadi, B. J. Berne, and D. Forster, Phys. Rev. A **3**, 1462 (1970).

[3] B. J. Alder and T. E. Wainwright, Phys. Rev. A **1**, 18 (1970).

[4] R. Zwanzig and M. Bixon, Phys. Rev. A **2**, 2906 (1970).

[5] A. Widom, Phys. Rev. A **3**, 1394 (1971). In this paper the linear momentum correlation function for a macroscopic sphere with stick boundary conditions is calculated. Actually, this treatment is included as a special case in Ref. 4.

[6] L. Landau and E. M. Lifshitz, *Fluid Mechanics* (Addison-Wesley, Reading, Mass., 1959).

[7] R. Kubo, Rept. Progr. Phys. **29**, 235 (1966).

[8] G. Harp and B. J. Berne, Phys. Rev. A **2**, 1462 (1970).

[9] R. Zwanzig and T. Nee, J. Chem. Phys. **52**, 6353 (1970).

[10] Roy G. Gordon and T. J. Messenger (preprint).