

# A hydrodynamic theory of the angular velocity correlation function with arbitrary slip boundary conditions

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In a recent publication in this journal<sup>1</sup> we presented a hydrodynamic theory of the angular velocity correlation function based on the frequency-dependent friction coefficient for a rotating sphere with stick boundary conditions at the surface. This comment will show how this treatment can be extended to the case of partially slippery boundaries.

To allow arbitrary slip at the surface of the rotating sphere, the boundary condition given by Eq. (2) of Ref. 1 is replaced by

$$\mathbf{a}_r \cdot \boldsymbol{\sigma} \cdot \mathbf{a}_\nu = \frac{\beta}{R} (\mathbf{v}_\omega - \boldsymbol{\Omega}_\omega \times \mathbf{R}) \cdot \mathbf{a}_\nu, \quad (1)$$

where  $\beta$  is a dimensionless parameter which specifies the degree of slip,  $\beta = \infty$  corresponds to the complete stick limit of Ref. 1, and  $\beta = 0$  corresponds to pure slip (i.e., free rotation). This method of generalizing the boundary conditions is due to Basset<sup>2</sup> and was successfully used by Zwanzig and Bixon<sup>3</sup> in their calculation of the velocity correlation function.

A straightforward calculation gives the following result for the Laplace transform of the rotational friction coefficient (in the reduced units of Ref. 1):

$$\zeta(\beta, p) = \left( \frac{1 + \sqrt{p}}{(1 + 3\eta/\beta)(1 + \sqrt{p}) + p\eta/\beta} \right) \zeta(p), \quad (2)$$

where  $\zeta(p)$  is the pure stick result of Eq. (4), Ref. 1,

$$\zeta(p) = \zeta_R \left( 1 + \frac{p}{3(1 + \sqrt{p})} \right), \quad \zeta_R = 8\pi\eta R^3$$

The Laplace transform of the angular velocity correlation function (AVCF) may be expanded asymptotically as done in Ref. 1 to find the short time behavior of the AVCF, which is given by

$$C(t) - 1 - \frac{2\beta}{\lambda} t + O(t^2), \quad \lambda = \frac{\kappa\rho}{\rho S}. \quad (3)$$

The behavior at short times of the purely viscous AVCF with complete stick was found in Ref. 1 to be

$$C(t) - 1 - \frac{4}{\lambda\sqrt{\pi}} \sqrt{t} + O(t), \quad (4)$$

showing that slip drastically alters the short time behavior. A further interesting result is found if viscoelastic response is introduced by the simple single relaxation time model used in Ref. 1, where the replacement

$$\eta \rightarrow \eta \frac{1}{1 + \gamma p} \quad (5)$$

is made. The short time behavior of the AVCF becomes

$$C(t) - 1 - \frac{2}{\lambda} \frac{1}{\sqrt{\gamma + \eta/\beta}} t + O(t^2). \quad (6)$$

As one would expect from other theories,<sup>4</sup> the introduction of partially slippery boundary conditions and viscoelastic response does not change the long time behavior of the AVCF which is given by

$$C(t) \sim \frac{\lambda}{24\sqrt{\pi}} \left( \frac{R}{\nu t} \right)^{5/2} \quad (\text{in real time}).$$

The full time dependence of the AVCF may be found as in Ref. 1. We do not give those results here.

The initial decay given by Eq. (6) contains two parameters,  $\gamma$  and  $\beta$ , which cannot be uniquely determined by requiring agreement with the exact collision dynamics as done previously. An alternative is given by Theodosopulu and Dahler,<sup>5</sup> who find

$$\eta(p) = \eta \left( \frac{1 + \gamma_2 p}{1 + \gamma_1 p} \right),$$

from the kinetic theory of a dense rough sphere fluid, with  $\eta$ ,  $\gamma_1$ , and  $\gamma_2$  expressed in terms of microscopic quantities. In our earlier investigations we rejected this model because it gave the unphysical initial decay of Eq. (4) in the limit of complete stick. With partial slip, however, the initial decay of Eq. (3) is found. Use of this viscoelastic model and the expression for the initial decay given by the exact binary collision dynamics would allow a completely *ab initio* calculation of the AVCF. This approach has recently been taken by Hynes, Kapral, and Weinberg.<sup>6</sup> However, we have found<sup>7</sup> that one cannot obtain agreement at intermediate times with molecular dynamics by requiring the hydrodynamic theory to fit the exact initial decay.

The effect of arbitrary slip on the rotational diffusion coefficient is easily found from the zero frequency limit of Eq. (2):

$$D_R = \frac{kT}{\zeta(\beta, 0)} = \frac{kT}{\zeta_R} \left( 1 + \frac{3\eta}{\beta} \right). \quad (7)$$

Equation (7) exhibits the correct behavior in the pure stick and slip limits. A possible application of these results is to molecular dynamics simulations of the partially rough sphere model recently proposed by Berne and Montgomery,<sup>8</sup> currently in progress.

<sup>1</sup>J. A. Montgomery, Jr. and B. J. Berne, J. Chem. Phys. (in press).

<sup>2</sup>A. B. Basset, *A Treatise on Hydrodynamics* (Dover, New York, 1961), Vol. 2.

<sup>3</sup>R. Zwanzig and M. Bixon, Phys. Rev. A 2, 2005 (1970).

<sup>4</sup>N. K. Ailawadi and B. J. Berne, IUPAP Conference on Statistical Physics, Chicago, March, 1971.

<sup>5</sup>M. Theodosopulu and J. S. Dahler, J. Chem. Phys. 60, 4048 (1974).

<sup>6</sup>Raymond Kapral (private communication).

<sup>7</sup>B. J. Berne, J. A. Montgomery, Jr., and C. S. Pangali (unpublished).

<sup>8</sup>B. J. Berne and J. A. Montgomery, Jr., Mol. Phys. 32, 363 (1976).

## Comment: The bound ${}^3\Sigma_u^+$ excited level of $H_3^+$

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Schaad and Hicks<sup>1</sup> (SH) have recently published a CI study of low lying electronic states of  $H_3^+$  that proved the existence of a stable  ${}^3\Sigma_u^+$  state (symmetry group  $D_{\infty h}$ ). The analysis of  $E({}^3\Sigma_u^+)$  as computed by SH revealed two interesting features:

(a) an extremely large coupling force constant  $k_{12} = 0.051$  a.u. as compared to  $k_1 = 0.030$  a.u., and

(b) it further appeared "that the bonds of  $H_3^+$  ( ${}^3\Sigma_u^+$ ) are more difficult to stretch than to compress, contrary to what one expects from a Morse approximation to the potential." We found these results of SH interesting enough to justify a more accurate computation of  $E({}^3\Sigma_u^+)$  in order to check their validity.

The energy and wavefunction of the  ${}^3\Sigma_u^+$  state of  $H_3^+$  were computed with a recently developed MC-SCF procedure<sup>2</sup> which determines the wavefunction in its NO expansion. Convergence ( $|\Delta E| < 10^{-7}$  a.u.) was reached within 7 iterations at most for the present case. Each iteration requires roughly the computational labor of a conventional HF iteration.

The computations were performed with an extended Gaussian basis set: a Huzinaga<sup>3</sup> 6s basis, contracted (3, 1, 1, 1), augmented by two *p* sets ( $\eta = 0.199, 0.660$ ) and a *d* set<sup>4</sup> ( $\eta = 0.651$ ). The orbital exponents were determined from minimization of the total energy at the SH equilibrium distance  $R_e = 2.457$  a.u. We have checked that this basis is flexible enough to make a re-optimization of  $\eta$ 's—at geometries different from the equilibrium—superfluous, since such a procedure changes, e.g., the stretching force constant by 0.4% at most. SH have used a smaller Gaussian basis than we did (4s for the surface, 4s 1p for the equilibrium), but optimized certain basis set parameters at each geometry which appears to be a rather costly procedure.<sup>1</sup> The present computations required between 12 and 20 min. per point depending on molecular symmetry (UNIVAC 1108 IO+CPU, using double precision arithmetic).

We first determined the equilibrium distance  $R_e$  and the corresponding electronic energy, including internuclear repulsion, results of SH<sup>1</sup> are given in parenthesis

$$R_e({}^3\Sigma_u^+ H_3^+) = 2.4568 \text{ a.u. } (2.457) \quad (1)$$

$$E({}^3\Sigma_u^+ H_3^+) = -1.1156787 \text{ a.u. } (1.114219) . \quad (2)$$

For comparison we also computed the energy of the  ${}^3\Sigma_u^+$  state of  $H_2$ ,  $E({}^3\Sigma_u^+ H_2) = -0.896410$ , and the  ${}^2\Sigma_g^+$  of  $H_2^+$ ,  $E({}^2\Sigma_g^+ H_2^+) = -0.602309$ , both at  $R = 2$  a.u. These energies are only 0.4 kcal/mol and 0.2 kcal/mol poorer than the virtually exact ones reported in the literature.<sup>5,6</sup> Since our basis set was optimized for the  $H_3^+$  case, we are confident that the energy given in Eq. (2) is at most 0.4 kcal/mol—probably less than 0.2 kcal/mol—higher than the exact one. Combining our computed energies with that of H (1s) ( $-0.499940$  a.u. with the 6s basis<sup>3</sup>) we get  $\Delta E$  for the Reaction (3)



$$\Delta E = -0.013430 \text{ a.u. } = -8.43 \text{ kcal/mol} . \quad (4)$$

TABLE I. Energy of  $H_3^+$  ( ${}^3\Sigma_u^+$ ) along symmetry coordinates.

	This work	SH
$\Delta r_1 = \Delta r_2$ <sup>a</sup> $\sigma_g^+$ mode	$\Delta E(10^{-7} \text{ a.u.})$	
-0.4	128716	...
-0.2	27184	...
-0.1	6269	4994
-0.05	1507	1299
-0.025	370	332
0.025	355	344
0.05	1395	1404
0.1	5373	5853
0.2	19965	...
0.4	69290	...
$\Delta r_1 = -\Delta r_2$ <sup>b</sup> $\sigma_u^+$ mode		
0.1	890	603
0.05	218	148
0.025	54	37
$\Delta x_1 = \Delta x_3 = -2\Delta x_2$ <sup>c</sup> $\pi_u$ mode		
0.075	1478	1716
0.0375	369	429
0.01875	92	107

$${}^a Q_1 = (\Delta r_1 + \Delta r_2) / \sqrt{2}.$$

$${}^b Q_3 = (\Delta r_1 - \Delta r_2) / \sqrt{6}.$$

$${}^c Q_{2a} = (\Delta x_1 - 2\Delta x_2 + \Delta x_3) / \sqrt{6}.$$