JOURNAL OF CHEMICAL PHYSICS VOLUME 110, NUMBER 3 15 JANUARY 1999

COMMENTS

Comment on ''Dynamics of solvated ion in polar liquids: An interaction-site-model description'' [J. Chem. Phys. 108, 7339 (1998)]

Ranjit Biswas and Biman Bagchi[a)]
Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore, 560012, India

(Received 8 June 1998; accepted 5 October 1998)

[S0021-9606(99)50302-4]

Recently Chong and Hirata[1] have discussed an interesting molecular approach for friction on a solvated ion in a dipolar liquid. We have the following comments on this paper.

(1) Note that Eq. (2.9) of the Chong–Hirata paper[1] is essentially the same as presented earlier by us in several places. See, for example, Eq. (2) of Ref. 2, Eq. (9) of Ref. 3 and Eq. (3) of Ref. 4. As to the best of our knowledge, this self-consistent equation was presented, *for the friction on an ion*, for the *first* time in Ref. 2. We have mentioned earlier that this is a general equation which can be derived by several approaches. We were, therefore, surprised that no due acknowledgement was given to our work.

Actually, there are two stages in the calculation of the total friction on a moving ion. The first stage involves the formulation of a mode coupling type theory. This was already accomplished in Refs. 5–7. The second stage is the calculation of the correlation functions. It is here that Hirata and Chong have made a meaningful contribution by using the interaction site model to describe the correlation functions.

(2) About our work,[2–4] Chong and Hirata made the critical observation that ''their theory does not answer the question of how the Stokes and dielectric frictions interplay because it *disregards the microscopic nature of the Stokes friction*.'' This statement is not correct. The bare friction can also be calculated from the mode coupling theory by treating the ion as a fictitious neutral solute of the same size. We have stated clearly that we have approximated the bare friction (due to the short range interactions) by the hydrodynamic term because the latter provides a *reasonable* numerical approximation. There was no *disregard*. Actually, the bare friction has been calculated elsewhere.[6,7] There is nothing new about this.

(3) In fact, Chong and Hirata also did not include the hydrodynamic term. The simultaneous inclusion of the microscopic and the hydrodynamic terms is a difficult and tricky problem which has been solved only recently.[5] Actually, one cannot include the hydrodynamic term by the *conventional* molecular approach which considers *only* the density relaxation [see Eq. (2.4) of Chong and Hirata]. The Stokes term comes from an *entirely* different source, from the transverse current mode. We have shown recently that the proper form of the friction is given by the following expression:[5]

$$\frac{1}{\zeta}=\frac{1}{\zeta_{bin}+\zeta_{\rho\rho}+\zeta_{mic,DF}}+\frac{1}{\zeta_{hyd}+\zeta_{hyd,DF}}, \tag{1}$$

where ζ_{bin} and $\zeta_{\rho\rho}$ are the binary and the collective solvent number density (ρ) fluctuation contributions, respec-tively.[5–7] The details regarding the calculation of these two microscopic quantities are described elsewhere.[5–7] $\zeta_{mic,DF}$ represents the friction which originates from the coupling of the ionic field with the orientational solvent polarization mode. On the other hand, ζ_{hyd} and $\zeta_{hyd,DF}$ are the hydrodynamic friction (without the polar contribution) and the hydrodynamic (polarization current) dielectric friction. The expressions for $\zeta_{mic,DF}$ and $\zeta_{hyd,DF}$ are given below:[2–4,7]

$$\zeta_{mic,DF}=\frac{2k_BT\rho}{3(2\pi)^2}\int_0^\infty dt \times\int_0^\infty d\mathbf{k}k^2 S_{ion}(k,t)|c_{id}^{10}(k)|^2 S_{solvent}^{10}(k,t), \tag{2}$$

where $c_{id}^{10}(k)$ is the wavenumber (k) dependent (10) component of the ion–dipole direct correlation function. This is a coupling parameter which couples the ion dynamic structure factor, $S_{ion}(k,t)$ with the orientational solvent dynamic structure factor, $S_{solvent}^{10}(k,t)$. k_BT is, as usual, the Boltzmann's constant times the absolute temperature. The polarization current (hydrodynamic) friction is given by[5,7]

$$\zeta_{hyd,DF}(t)=\frac{1}{3\rho(2\pi)^3}\int d\mathbf{k}S_{ion}(k,t)\frac{2\hat{f}(k)}{k^2}C_{tt}(k,t), \tag{3}$$

where $\hat{f}(k)$ denotes the wavenumber dependent form factor and C_{tt} the solvent polarization current auto correlation function. We refer the interested reader to Ref. 5 for a detailed discussion and derivation of Eqs. (1)–(3).

(4) We would like to stress that while the Stokes term and the expressions for dielectric friction derived by Hubbard and Onsager[8] and by Zwanzig[9] have the origin in the solvent polarization current *only*, the molecular expression used by Wolynes[10] and by us[2–4,11] and others arises from the systematic consideration of both the microscopic structure and dynamics of the ion–solvent composite system.

(5) While Chong and Hirata[1] wrote that we ''claimed'' good agreement, the fact is that we *did* get good agreement with known results, without any adjustable parameter. The

© 1999 American Institute of Physics

Downloaded 08 Sep 2010 to 122.172.63.253. Redistribution subject to AIP license or copyright; see http://jcp.aip.org/about/rights_and_permissions

inconsistency discussed above does not affect the numerical results for two reasons. First, for small ions, the exact magnitude of the bare term becomes insignificant because the dielectric friction dominates the total friction. For large ions, dielectric friction itself is not important. Thus, the maximum was recovered correctly.

[a] Electronic mail: bbagchi@sscu.iisc.ernet.in; Fax: 91 80 33 41 683; 91 80 33 11 310.

[1] S. H. Chong and F. Hirata, J. Chem. Phys. **108**, 7339 (1998).
[2] R. Biswas, S. Roy, and B. Bagchi, Phys. Rev. Lett. **75**, 1098 (1995).
[3] R. Biswas and B. Bagchi, J. Chem. Phys. **106**, 5587 (1997).
[4] R. Biswas and B. Bagchi, J. Am. Chem. Soc. **119**, 5946 (1997).
[5] B. Bagchi, J. Chem. Phys. **109**, 3989 (1998).
[6] L. Sjogren and A. Sjolander, J. Phys. C **12**, 4369 (1979).
[7] S. Bhattacharyya and B. Bagchi, J. Chem. Phys. **106**, 1757 (1996); **106**, 7262 (1997).
[8] J. B. Hubbard and P. G. Wolynes, in *The Chemical Physics of Solvation*, edited by R. Dogonadze *et al*. (Elsevier, New York, 1988), Part C, Chap 1, p. 33; J. B. Hubbard and L. Onsager, J. Chem. Phys. **67**, 4850 (1977).
[9] R. Zwanzig, J. Chem. Phys. **38**, 1603 (1963); **52**, 3625 (1970).
[10] P. G. Wolynes, Annu. Rev. Phys. Chem. **31**, 345 (1980); P. G. Wolynes, J. Chem. Phys. **68**, 473 (1978).
[11] B. Bagchi and R. Biswas, Acc. Chem. Res. **31**, 181 (1998).

Downloaded 08 Sep 2010 to 122.172.63.253. Redistribution subject to AIP license or copyright; see http://jcp.aip.org/about/rights_and_permissions