

PRELIMINARY COMMUNICATION

The distribution of fluctuations of the total dipole moment in polar liquids

By P. G. KUSALIK

Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, B3H 4J3, Canada

(Received 21 June 1993; accepted 12 July 1993)

The distribution of fluctuations of the total dipole moment in polar liquids is characterized. The functional form of the probability distribution function, $P(g)$, where g is proportional to the square of the total moment and its average value is directly related to the static dielectric constant, is empirically determined. A formal justification of the functional form is then developed and implications to the calculation of the dielectric constant in computer simulations are discussed.

The dielectric properties of polar liquids, particularly the static dielectric constant ϵ , are fundamental characteristics of these systems [1]. Unfortunately, the determination of these properties by computer simulation has presented both conceptual [2–7] and computational difficulties [7–16]. Many of the problems associated with the treatment of the boundary conditions have now been resolved, yet many important questions concerning the influences of the boundary conditions and finite-size samples have remained at least partially unanswered [14–16]. Furthermore, although reasonably precise values for ϵ for highly polar liquids (such as water) can be determined with rather long simulations, the results obtained may still contain non-trivial systematic errors due to the effects of system size and boundary conditions (for examples, see [13–15]). Clearly, there is a need for more computationally efficient routes to ϵ and for an increased understanding of the influences of sample size and boundary conditions upon the dielectric properties of polar liquids.

The traditional means of obtaining the static dielectric constant from a computer simulation has been from the average fluctuations in the total dipole moment of the system, M , through the standard relationship (valid for both reaction-field and periodic boundary conditions [3, 5])

$$\frac{(\epsilon - 1)(2\epsilon_{\text{RF}} + 1)}{2\epsilon_{\text{RF}} + \epsilon} = \frac{4\pi}{3V} \frac{\langle M^2 \rangle}{kT} = 3y\langle g \rangle, \quad (1)$$

in which ϵ_{RF} is the dielectric constant of the continuum surrounding our spherical sample (e.g., $\epsilon_{\text{RF}} = 1$ corresponds to an isolated system), M is $|\mathbf{M}|$, V is the volume, $y = 4\pi\rho\mu^2/9kT$ and

$$g = \frac{M^2}{N\mu^2}, \quad (2)$$

where $\rho = N/V$ is the number density and μ^2 is the square of the molecular dipole moment. We point out that g as defined by equation (2) is an instantaneous rather than an average quantity.

Although other approaches have been attempted, such as applied field simulations [9, 11, 16], little success has been achieved in identifying a clearly superior computational route to ϵ , with perhaps the exception of the very recent work of Chandler and co-workers [13]. Our interest in trying to develop more computationally efficient routes to the static dielectric constant and in improving our understanding of the effects of finite sample size and boundary conditions has recently brought our focus of attention back onto the fluctuations in M . In this communication we will briefly report recent results for the distribution of values for g (and hence of M or M^2) and will formally characterize this probability distribution function; implications to the determination of the static dielectric constant will also be discussed.

The dipolar soft-sphere model and the general molecular dynamics simulation methodology used in the present study have been described in detail previously [14]. A much more complete presentation and analysis of the current results will be given in a forthcoming article [17]. Here it is sufficient to note that this dipolar soft-sphere fluid, characterized by a reduce density $\rho^* = 0.8$, a reduced temperature $T^* = 1.35$, and a reduced dipole moment $\mu^* = 2.0$, has been the subject of extensive studies reported earlier [14–16], from which an estimate of 98 ± 2 was obtained for the infinite system dielectric constant. As in our previous work, periodic boundary conditions (PBC) have been employed with the required lattice sums being evaluated with the Ewald summation technique [18]. The distribution functions reported here were obtained from trajectories of 500 000 timesteps.

As M is an extensive property, its probability distribution function, $P(M)$, is not convenient for comparing results from systems of different size. Rather, we focus on $P(g)$,[†] where $P(g) dg$ gives the probability of observing the system with a value of g between g and $g + dg$. Data for $P(g) * \Delta g$ were determined directly in each simulation from a simple histogram for g with a bin width, Δg , of 0.25. Figure 1 shows curves for $P(g) * \Delta g$ for samples of 108 and 500 dipolar soft-spheres at $\epsilon_{\text{RF}} = 10$ and ∞ ; we find that the value of ϵ_{RF} can have a large impact upon the distribution of values of g recorded during the simulation, as we might expect. Moreover, effects due to sample size are also evident in figure 1. When our data are presented as the function $P(M)$, the curves obtained are qualitatively very similar to those of Chandler (see figure 4 of [13]).

In trying to characterize a functional form for $P(g)$, it was found empirically that plots of $\ln [P(g)/g^{1/2}]$ versus g demonstrate linear behaviour, as exemplified by our 108 and 500 particle samples in figure 2. Deviations from linearity (most evident for small samples and large ϵ_{RF}) are a finite system size effect, and will be discussed fully in our later article [17].

The dependence of $P(g)$ upon ϵ_{RF} is perhaps most clearly demonstrated by considering the ratio,

$$R(\epsilon'', \epsilon') = \frac{P(g; \epsilon_{\text{RF}} = \epsilon'')}{P(g; \epsilon_{\text{RF}} = \epsilon')}, \quad (3)$$

[†] We remark that this isotropic function is sufficient for the present system since it is well known from solid-state nuclear magnetic resonance [19] that the dipole–dipole interaction cannot distinguish between cubic and true spherical symmetry. Hence our sample should possess *no* anisotropy, a fact which we have confirmed numerically [17].

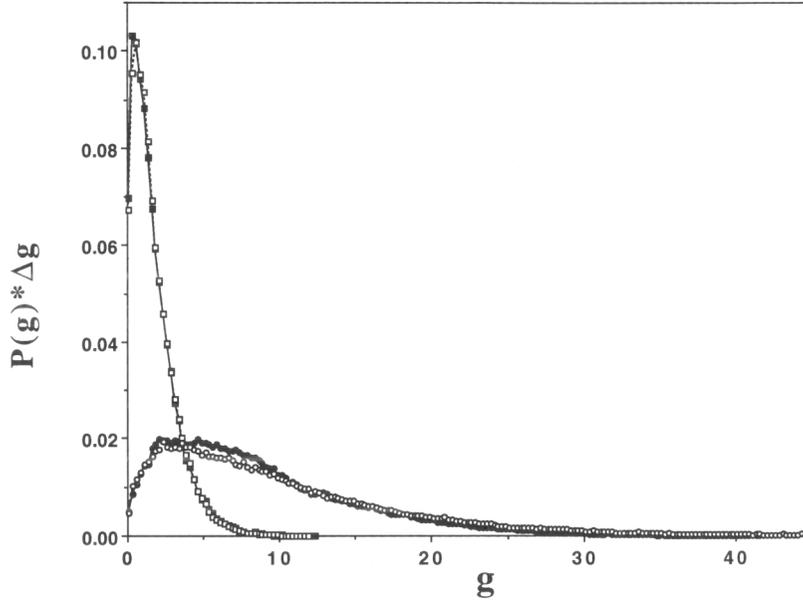


Figure 1. Probability distribution function, $P(g)$. The dots and open circles are, respectively, results for $P(g) * \Delta g$ for systems of 108 and 500 dipolar soft spheres at $\epsilon_{\text{RF}} = \infty$, while the solid and open squares are the respective values obtained at $\epsilon_{\text{RF}} = 10$.

of two distributions at two values, ϵ'' and ϵ' , of ϵ_{RF} . In figure 3 the logarithm of R is shown for our $N = 108$ and 500 systems for $\epsilon'' = \infty$ and $\epsilon' = 10$ and we find that $P(g)$ scales exponentially with a change in ϵ_{RF} .

We begin our formal analysis of $P(g)$ with our empirically determined functional form

$$P(g) = Ag^{1/2} \exp(-\kappa g), \quad (4a)$$

where κ is just the slopes of the lines in figure 2 and normalization requires that

$$A = \frac{2\kappa^{3/2}}{\pi^{1/2}}. \quad (4b)$$

Then inserting this form into the definition

$$\langle g \rangle = \int_0^{\infty} gP(g) dg \quad (5)$$

and integrating, it follows that

$$\langle g \rangle = \frac{3}{2\kappa}. \quad (6)$$

Thus the value of κ and the average value of g are trivially related and we can rewrite equation (1) as

$$\frac{(\epsilon - 1)(2\epsilon_{\text{RF}} + 1)}{2\epsilon_{\text{RF}} + \epsilon} = \frac{2\pi\rho\mu^2}{\kappa kT}. \quad (7)$$

In order to proceed we first recall that $P(g)$ undergoes a simple exponential scaling for any change in ϵ_{RF} ; hence we assume that κ is the sum of two terms, γ

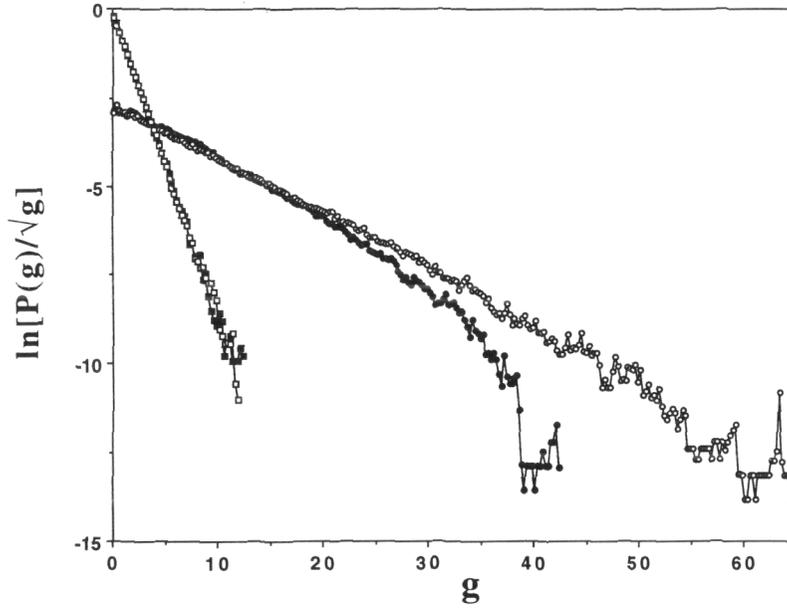


Figure 2. The logarithm of $P(g)/g^{1/2}$. The symbols are defined as in figure 1.

and δ , and write that

$$P(g) = Ag^{1/2} \exp(-\gamma g) \exp(-\delta g), \quad (8)$$

where $\delta = \delta(\epsilon_{\text{RF}})$ is the boundary dependent term and γ is independent of ϵ_{RF} . Further, we define γ to be the value of κ for the true infinite system (i.e., $\gamma = \kappa(\epsilon_{\text{RF}} = \epsilon)$) so that

$$P(g; \epsilon_{\text{RF}} = \epsilon) = Ag^{1/2} \exp(-\gamma g). \quad (9)$$

Now for any polar system in PBC where the sample being considered is spherical the pair interaction between the particles i and j may be written as [18]

$$u_{ij}(\epsilon_{\text{RF}}) = u_{ij}(\epsilon_{\text{RF}} = 1) - \frac{2(\epsilon_{\text{RF}} - 1)}{2\epsilon_{\text{RF}} + 1} \frac{4\pi}{3V} (\boldsymbol{\mu}_i \cdot \boldsymbol{\mu}_j), \quad (10)$$

in which $u_{ij}(\epsilon_{\text{RF}} = 1)$ is just the pair potential of the particles in an isolated sample and the second term arises due to the interaction of the sample with the surrounding dielectric continuum, where $\boldsymbol{\mu}_i$ is the dipole moment of i . The change in energy of the system due to a change *only* in the continuum dielectric constant from ϵ' to ϵ'' can be expressed as

$$\Delta U(\epsilon'', \epsilon') = \frac{1}{2} \sum_{i,j} u_{ij}(\epsilon'') - \frac{1}{2} \sum_{i,j} u_{ij}(\epsilon'), \quad (11)$$

and using equation (10) and simplifying we immediately have

$$\Delta U(\epsilon'', \epsilon') = \frac{2\pi M^2}{V} \left(\frac{1}{2\epsilon'' + 1} - \frac{1}{2\epsilon' + 1} \right). \quad (12)$$

An equivalent result can be obtained for large samples in reaction field (RF) boundary conditions as we will show in our forthcoming article [17]. The ratio of the probabilities

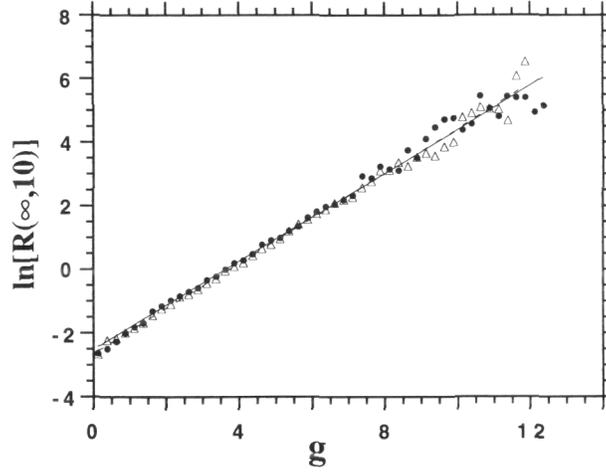


Figure 3. The logarithm of the ratio, $R(\infty, 10)$. The dots and triangles represent results for $N = 108$ and 500 , respectively. The solid and dashed lines are the least square linear fits discussed in the text.

of two identical (but arbitrary) configurations of a sample subject to two different boundary conditions, ϵ'' and ϵ' , will be given by (cf. equation (3))

$$R(\epsilon'', \epsilon') = \exp [-\beta \Delta U(\epsilon'', \epsilon')]. \quad (13)$$

Substitution of equations (2) and (12) immediately yields that

$$\ln [R(\epsilon'', \epsilon')] = \frac{-2\pi\rho\mu^2}{kT} \left(\frac{1}{2\epsilon'' + 1} - \frac{1}{2\epsilon' + 1} \right) g. \quad (14)$$

The slopes of the least square linear fits to the data for $\ln [R(\infty, 10)]$ in figure 3 are 0.691 and 0.707, respectively, for the 108 and 500 particle systems (0.717 and 0.706 if only points in the range $g = 0$ to 7 are used). The value of 0.709 predicted by equation (14) is in *excellent* agreement with our numerical results. From equations (3), (8) and (14), and our definitions of γ and δ , it follows trivially that

$$\delta(\epsilon_{RF}) = \frac{2\pi\rho\mu^2}{kT} \left(\frac{1}{2\epsilon_{RF} + 1} - \frac{1}{2\epsilon + 1} \right). \quad (15)$$

It should be noted that equation (15) can be shown to be entirely consistent with equation (7).

In order to develop a relationship for γ , and hence to complete our characterization of $P(g)$, we begin by considering the probability of observing a total moment of magnitude M ,

$$\mathcal{P}(M) \propto \exp [-\beta F(M)], \quad (16)$$

where $F(M)$ is the Helmholtz free energy of the system. Using macroscopic electrostatic arguments, Frölich (cf. equation 7.19 of [20]) has shown that for a large spherical sample of volume V embedded in an infinite isotropic system of the same material with dielectric constant ϵ ,

$$F(M) = F_0 + \frac{2\pi M^2}{V} \frac{3\epsilon}{(2\epsilon + 1)(\epsilon - 1)}, \quad (17)$$

in which F_0 is just the free energy for $M = 0$. Thus, the probability of the sample having a total moment with a magnitude between M and $M + dM$ is

$$\mathcal{P}(M) = B \exp\left(\frac{-2\pi M^2}{V} \frac{3\epsilon}{(2\epsilon + 1)(\epsilon - 1)}\right) 4\pi M^2 dM, \quad (18)$$

where B is the normalization constant. Then, since the system is isotropic

$$\mathcal{P}(M) = P(M) dM = P(\mathbf{M}) d\mathbf{M}, \quad (19)$$

and we can immediately define the two probability distribution functions

$$P(M) = 4\pi M^2 B \exp(-aM^2) \quad (20a)$$

and

$$P(\mathbf{M}) = B \exp(-aM^2), \quad (20b)$$

where

$$a = \frac{2\pi}{VkT} \frac{3\epsilon}{(2\epsilon + 1)(\epsilon - 1)}. \quad (20c)$$

Again, it is convenient to express the probability in terms of g , and one can directly obtain from equations (2) and (18) that

$$P(g) = Cg^{1/2} \exp\left(\frac{-2\pi\rho\mu^2}{kT} \frac{3\epsilon}{(2\epsilon + 1)(\epsilon - 1)} g\right), \quad (21)$$

which we can compare with equation (9) to give that

$$\gamma = \frac{2\pi\rho\mu^2}{kT} \frac{3\epsilon}{(2\epsilon + 1)(\epsilon - 1)}. \quad (22)$$

Clearly, equations (7) and (22) are self-consistent when $\epsilon_{\text{RF}} = \epsilon$.

The formal results given here should be *universally* applicable to any ‘large’ spherical sample of a polar liquid. Numerically this has been confirmed not only in simulations of dipolar soft-sphere fluids, but also for models of water and methanol [17]. In our forthcoming article [17] we will discuss in detail the effects of system size and boundary conditions (i.e., RF versus PBC) upon $P(g)$, and hence the static dielectric constant. Knowledge of the functional form of $P(g)$ can now be easily exploited to improve the statistical sampling in simulations with either biased sampling [18] or windowing [13] type techniques. In [17] we will demonstrate that only a fraction of the full distribution need be sampled (with considerable computational savings) to determine a reasonably precise estimate for the dielectric constant.

I wish to acknowledge the Australian National University and the Research School of Chemistry for their support during my visit. I am grateful for the financial support of the Natural Sciences and Engineering Research Council of Canada, and I wish to thank Drs P. Attard, I. M. Svishchev and M. E. Mandy for helpful discussions.

References

- [1] HANSEN, J. P., and McDONALD, I. R., 1986, *Theory of Simple Liquids*, 2nd edition (Academic).

- [2] DE Leeuw, S. W., PERRAM, P. W., and SMITH, E. R., 1986, *Ann. Rev. phys. Chem.*, **37**, 245.
- [3] PATEY, G. N., LEVESQUE, D., and WEIS, J. J., 1982, *Molec. Phys.*, **45**, 733.
- [4] NEUMANN, M., and STEINHAUSER, 1980, *Molec. Phys.*, **39**, 437; *Chem. Phys. Lett.*, 1983, **95**, 417.
- [5] NEUMANN, M., 1986, *Molec. Phys.*, **57**, 97.
- [6] NEUMANN, M., 1983, *Molec. Phys.*, **50**, 841.
- [7] ALDER, B. J., and POLLOCK, E. L., 1981, *Ann. Rev. phys. Chem.*, **32**, 311; 1980, *Physica A*, **102**, 1.
- [8] NEUMANN, M., STEINHAUSER, O., and PAWLEY, G. S., 1984, *Molec. Phys.*, **52**, 97; NEUMANN, M., 1985, *J. chem. Phys.*, **82**, 5663; *Ibid*, 1986, **85**, 1567.
- [9] ADAMS, D. J., and ADAMS, E. M., 1981, *Molec. Phys.*, **42**, 907.
- [10] LEVESQUE, D., and WEIS, 1984, *Physica A*, **125**, 270.
- [11] ALPER, H. E., and LEVY, R. M., 1989, *J. chem. Phys.*, **91**, 1242.
- [12] WATANABE, K., and KLEIN, M., 1989, *Chem. Phys.*, **131**, 157.
- [13] KURTOVIC, Z., MARCHI, M., and CHANDLER, D., 1993, *Molec. Phys.*, **78**, 1155.
- [14] KUSALIK, P. G., 1990, *J. chem. Phys.*, **93**, 3520.
- [15] KUSALIK, P. G., 1991, *Molec. Phys.*, **73**, 1349.
- [16] KUSALIK, P. G., 1993, *Molec. Phys.*, in press.
- [17] KUSALIK, P. G., MANDY, M. E., and SVISHCHEV, I. M., to be submitted.
- [18] ALLEN, M. P., and TILDESLEY, D. J., 1989, *Computer Simulation of Liquids* (Clarendon Press).
- [19] HEHRING, M., 1976, *High Resolution NMR Spectroscopy of Solids* (Springer-Verlag).
- [20] FRÖHLICH, H., 1958, *Theory of Dielectrics*, (Oxford University Press).