

# Response to “Comment on Nonlinear dielectric response of polar liquids” [J. Chem. Phys. XXX, XXXXX (2016)]

Dmitry V. Matyushov<sup>1</sup>

Department of Physics and School of Molecular Sciences, Arizona State University, PO Box 871504, Tempe, Arizona 85287<sup>a)</sup>

The problem raised in the Comment<sup>1</sup> is to how correctly calculate the Piekara coefficient<sup>2</sup> linking the field-induced alteration of the material dielectric constant to squared Maxwell electric field  $E$ ,  $\Delta\epsilon_E = \epsilon_E - \epsilon_s = -aE^2$ ;  $\epsilon_E$  is the field-dependent dielectric constant and  $\epsilon_s$  is its  $E = 0$  value. Derivations of such relations are typically based on statistical perturbation theories expanding the average dipole moment of the sample  $\langle \mathbf{M} \rangle_E$  in powers of the perturbation Hamiltonian<sup>3</sup>  $H' = -\mathbf{M} \cdot \mathbf{E}_0$ . Here  $\mathbf{M}$  is the dipole moment of a macroscopic sample and  $\mathbf{E}_0$  is the field of external charges applied along the  $z$ -axis of the laboratory frame ( $\langle \dots \rangle_E$  is the average in the presence of the field,  $\langle \dots \rangle_0$  is the average in the absence of the field, and  $\langle \mathbf{M} \rangle_0 = 0$ ).

The main difficulty of applying such fluctuation formulas is that the dielectric constant  $\epsilon_E - 1 = 4\pi \langle M \rangle_E / (VE)$  is given in terms of the Maxwell field, while perturbation expansions produce powers in  $E_0$  ( $V$  is the sample volume). Therefore, arriving at the material dielectric constant from fluctuation relations requires connecting  $E$  to  $E_0$ , which depends on the chosen geometry of the sample.<sup>4</sup>

In order to avoid the asymmetry of the response to  $E_0$ , early theories employed spherical samples polarized by the cavity field of the surrounding dielectric.<sup>4</sup> In contrast, slab geometry was used in Ref. 5. The Piekara coefficient is then proportional to  $\langle M_z^4 \rangle_0 - 3\langle M_z^2 \rangle_0^2$ , while the expression  $(1/5)\langle M^4 \rangle_0 - (1/3)\langle M^2 \rangle_0^2$  was previously derived for spherical samples.<sup>2,6-8</sup> The two equations are equal when the spherical symmetry of the sample is applied to  $\mathbf{M}$ , as is pointed out in the Comment. Correspondingly, the Piekara coefficient at constant volume (subscript “V”) becomes<sup>5</sup>  $a_V = (\beta\epsilon_s^2\Delta\epsilon_s^2/8\pi\rho)B_V$ , where  $\beta = 1/(k_B T)$ ,  $\Delta\epsilon_s = \epsilon_s - \epsilon_\infty$  and  $\rho = N/V$  is defined by the volume  $V$  and the number of molecules  $N$ . The reduced cumulant  $B_V = N[1 - \kappa_V]$  is given through either  $M_z$  or through  $\mathbf{M}$  as follows

$$\kappa_V = (3/5)\langle M^4 \rangle_0 / \langle M^2 \rangle_0^2 = \langle M_z^4 \rangle_0 / (3\langle M_z^2 \rangle_0^2). \quad (1)$$

Since dielectric constant is a local material property, employing either slab or spherical geometry is a matter of choice as long as the connection between  $E_0$  and  $E$  is provided. As an example, one can arrive at the Kirkwood-Onsager equation for a slab, which is typically derived for a spherical sample.<sup>4</sup> From the first-order perturbation theory, one gets  $\langle M_\alpha \rangle_E = \beta \langle M_\alpha^2 \rangle_0 E_{0\alpha}$  for Carte-

sian projections  $\alpha$ . For the slab geometry, the connection between  $E_0$  and  $E$  depends on whether the field is perpendicular or parallel to the slab plane:  $E_{0z} = \epsilon_s E_z$  and  $E_{0x} = E_x$ . Since the response to the Maxwell field,  $4\pi \langle M_\alpha \rangle_E = V(\epsilon_s - 1)E_\alpha$ , is invariant for an isotropic dielectric, one gets

$$\frac{(\epsilon_s - 1)(2\epsilon_s + 1)}{9\epsilon_s} = \frac{4\pi}{9} \frac{\beta \langle \mathbf{M}^2 \rangle_0}{V}, \quad (2)$$

where  $\mathbf{M}$  now is the total dipole moment of the slab. Here, for brevity, both the induced and permanent dipoles are included in  $\mathbf{M}$ . Mean-field theories can be constructed to separate fluctuations of the permanent and induced dipoles; the correlation Kirkwood factor appears in Eq. (2) from the variance of the permanent dipoles.<sup>9</sup>

Simulations of polar liquids typically involve spherical cutoff of electrostatic interactions and require collecting statistical averages in spherical samples. Equations of Ref. 5 can still be used to calculate the nonlinear response when averages are collected within a spherical cutoff. We illustrate this statement by two calculations: (i) two alternative ways to arrive at  $\kappa_V$  (Fig. 1a) and (ii) calculating binary correlations between powers of directional cosines  $e_{iz}$  of molecular dipoles appearing as separate terms in  $\langle M_z^4 \rangle$ . Figure 1b presents the test of one of the exact relations derived in Ref. 5 to separate binary from higher-order correlations

$$(5/N) \sum_{i \neq j=1}^N \langle e_{iz} e_{jz}^3 \rangle_0 = g_K - 1, \quad (3)$$

where  $g_K$  is the Kirkwood factor [Eq. (18) in Ref. 5, note the typo of a missing sum]. Closed circles in Fig. 1b refer to the left-hand side of this equation calculated by averaging over the simulation configurations. These results are compared to  $g_K - 1$  calculated from the dielectric constant (crosses) according to the Kirkwood-Onsager equation (Eq. (2)). The points in the plots are obtained by changing the dipole moment of the dipolar hard sphere, with the corresponding change in the dielectric constant of the fluid.

In the calculations reported here, the averages in Eqs. (1) and (3) are performed over the particles within the cutoff sphere of the radius equal to one-half the length of the cubic simulation box.<sup>10</sup> The values reported in Fig. 1b were obtained by extrapolating the simulated data to the infinite box size. Within the simulation uncertainties and differences in the length of the present and previous<sup>10</sup> simulations, the results are very close and support Eq.

<sup>a)</sup> Electronic mail: dmitrym@asu.edu

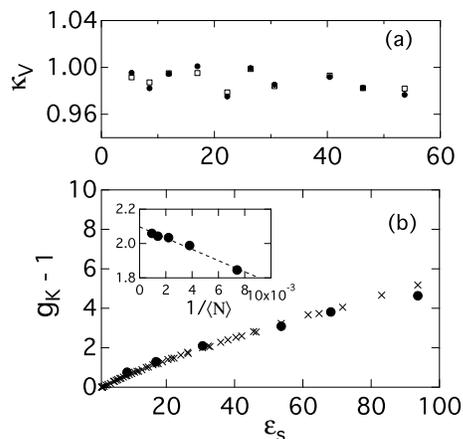


Figure 1. (a)  $\kappa_V$  calculated from  $M_z$  (closed points) and from  $\mathbf{M}$  (open points) according to Eq. (1) ( $N = 256$ ). (b) Left-hand side (circles) and right-hand side of Eq. (3) (crosses). The right-hand side is calculated from the dielectric constant according to the Kirkwood-Onsager equation (Eq. (2)) from simulation data reported in Ref. 10. The inset shows simulated  $g_K - 1$  vs the reciprocal number of particles within the spherical cutoff  $1/\langle N \rangle$  for  $\epsilon_s = 30.6$ . The dashed line is the linear regression. Its intercept for each point is reported in the main panel. All points refer to Monte Carlo simulations of fluids of  $N$  dipolar hard spheres with varying dipole moment.

(3). This relation can be viewed as an alternative route to calculate the Kirkwood factor. Further, two routes to calculate  $\kappa_V$  in Eq. (1) are equivalent within simulation uncertainties.

The traditional starting point for understanding the nonlinear dielectric response is the Langevin mean-field saturation function  $L(\beta m \chi_c E)$  describing the generally nonlinear effect of the cavity field  $\chi_c E$  on a single dipole  $m$ . The standard linear theory of dielectrics suggests<sup>4</sup>  $\chi_c = 3\epsilon_s/(2\epsilon_s + \epsilon_\infty)$ . The use of  $\epsilon_E$ , instead of  $\epsilon_s$ , in this equation<sup>6</sup> is highly questionable since the standard dielectric boundary problem, from which  $\chi_c$  is derived, does not hold when a dependence of the dielectric constant on the field is allowed. A consistent approach to the problem was suggested by Booth,<sup>11</sup> although not leading to a closed-form solution. However, more importantly, the entire mean-field approximation fails for nonlinear dielectric response and many-body correlations are required.<sup>5,7,8</sup>

The effect of temperature on the non-linear dielectric response deserves special comment. One can start with applying the linear expansion terms in the mean-field Langevin function to determine the bulk dielectric constant,  $\Delta\epsilon_s = (4\pi/3)\beta\mu^2\chi_c$ . The first nonlinear expansion term then specifies the mean-field Piekara coefficient

$$a^{\text{MF}} = (3\beta\epsilon_s\Delta\epsilon_s^2/20\pi\rho)(2\epsilon_s + \epsilon_\infty)^{-1}. \quad (4)$$

[Eq. (13) in Ref. 5], which yields  $\Delta\epsilon_E \propto T^{-1}$ . In contrast, traditional equations for the Piekara coefficient<sup>2,6</sup> produce  $\Delta\epsilon_E \propto T^{-3}$ . This is not merely a matter of

notation. For instance, when applied to water,  $a^{\text{MF}} \times 10^{15} \text{ (V/cm)}^2$  changes with temperature with the slope  $-0.1 \text{ K}^{-1}$  at  $T \simeq 300 \text{ K}$  according to Eq. (4), while the magnitude of the slope is much higher,  $-1.8 \text{ K}^{-1}$ , when Eq. (7.26) from Ref. 6 is used:  $a^{\text{MF}} = (4\pi g/45)\beta^3\mu^4$  with  $g = \epsilon_s^4(\epsilon_\infty + 2)^4/(2\epsilon_s + \epsilon_\infty)^2/(2\epsilon_s^2 + \epsilon_\infty^2)$ . The same calculation performed for acetonitrile yields a 40 times greater temperature slope in the second route compared to Eq. (4). Same arguments apply to the general expression for the Piekara coefficient  $a_V$  listed above, where  $\Delta\epsilon_E \propto T^{-1}$  appears as the explicit dependence on temperature.<sup>5</sup> The experimental evidence on this subject is scarce. Nevertheless, most recent measurements of low-temperature polar liquids<sup>12–14</sup> and of liquid crystals in their isotropic phase<sup>15</sup> point to  $\Delta\epsilon_E \propto T^{-1}$ , while  $\propto T^{-3}$  was reported in an earlier study of water.<sup>16</sup>

To summarize, the susceptibility to the field of external charges  $\mathbf{E}_0$  depends on the sample shape. However, experimental evidence suggests that the response of polarization to the Maxwell field  $\mathbf{E}$  is local and the corresponding dielectric constant is a local material property independent of the sample shape. Experiment suggests that independence of the sample shape can be extended to the field-dependent dielectric constant. One can use this evidence to derive susceptibilities connecting polarization to higher orders in the Maxwell field, which should be independent of the sample geometry and be solely the function of the material and  $\mathbf{E}$ . Derivations performed for different sample geometries should lead to equivalent results when nonlinear susceptibilities are expressed as expansions in powers of  $\mathbf{E}$ .

## REFERENCES

- <sup>1</sup>R. L. Fulton, J. Chem. Phys. **XXX**, XXXXX (2015).
- <sup>2</sup>A. Chelkowski, *Dielectric physics* (Elsevier Scientific Pub. Co., Amsterdam, 1980).
- <sup>3</sup>L. D. Landau and E. M. Lifshitz, *Electrodynamics of Continuous Media* (Pergamon, Oxford, 1984).
- <sup>4</sup>H. Fröhlich, *Theory of dielectrics* (Oxford University Press, Oxford, 1958).
- <sup>5</sup>D. V. Matyushov, J. Chem. Phys. **142**, 244502 (2015).
- <sup>6</sup>C. J. F. Böttcher, *Theory of Electric Polarization*, Vol. 1 (Elsevier, Amsterdam, 1973).
- <sup>7</sup>R. L. Fulton, J. Chem. Phys. **78**, 6865 (1983).
- <sup>8</sup>R. L. Fulton, J. Chem. Phys. **130**, 204503 (2009).
- <sup>9</sup>G. Stell, G. N. Patey, and J. S. Høye, Adv. Chem. Phys. **48**, 183 (1981).
- <sup>10</sup>D. R. Martin and D. V. Matyushov, J. Chem. Phys. **129**, 174508 (2008).
- <sup>11</sup>F. Booth, J. Chem. Phys. **23**, 453 (1955).
- <sup>12</sup>A. Drozd-Rzoska, S. J. Rzoska, and J. Ziolo, Phys. Rev. E **77**, 041501 (2008).
- <sup>13</sup>S. Rzoska, J. Ziolo, A. Drozd-Rzoska, J. L. Tamarit, and N. Veglio, J. Phys.: Condensed Matter **20**, 244124 (2008).
- <sup>14</sup>K. Koperwas, A. Grzybowski, K. Grzybowska, Z. Wojnarowska, and M. Paluch, J. Chem. Phys. **143**, 024502 (2015).
- <sup>15</sup>S. J. Rzoska, P. K. Mukherjee, and M. Rutkowska, J. Phys.: Condensed Matter **24**, 375101 (2012).
- <sup>16</sup>A. E. Davies, M. J. van der Sluijs, G. P. Jones, and M. Davies, J. Chem. Soc., Faraday Trans. 2 **74**, 571 (1978).