

# Nonlinear dielectric response of polar liquids

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The dielectric constant of a polar liquid in a strong electric field changes, in the lowest order, proportionally to the squared field magnitude. The proportionality coefficient (dielectric slope) is traditionally analyzed by mean-field models in terms of the saturation of alignment of individual dipoles as prescribed by the Langevin function. Only a decrease of the dielectric constant induced by the field is allowed by this model, in contrast to observations. Here, the dielectric slope is expressed in terms of the fourth-order cumulant of the liquid dipole moment. The cumulant is in turn separated into the two-particle dipolar correlations, expressed in terms of the Kirkwood factor and the liquid compressibility, and higher, triple and four-particle, dipolar correlations. The model allows both positive and negative dielectric slopes. Two-particle and higher-order correlations largely compensate each other. The analysis of experimental data suggests that dielectric slope gives experimental access to non-trivial triple and four-particle orientational correlations in polar liquids.

## I. INTRODUCTION

The polarization of a material is connected to a weak electric field by the linear dielectric susceptibility and the corresponding dielectric constant of the material  $\epsilon_s$ . At very strong fields, the susceptibility itself starts to depend on the field strength. The lowest-order correction to the linear susceptibility is quadratic in the Maxwell field  $E$ .<sup>1</sup> This implies that the dielectric decrement, i.e., the change of the dielectric constant in the field  $\epsilon_E$  relative to  $\epsilon_s$ , is proportional to  $E^2$  for typical electric field strengths employed experimentally,  $\Delta\epsilon_E = \epsilon_E - \epsilon_s \propto E^2$ . The ratio  $-\Delta\epsilon_E/E^2$ , known as the Piekara coefficient, has been measured for a number of polar liquids.<sup>2-6</sup>

The standard interpretation of the Piekara coefficient is that it represents dielectric saturation of a single dipole in the liquid, i.e., a generally nonlinear dependence of the average orientation of a dipole on the magnitude of the external field. This one-particle, or mean-field view of the nonlinear dielectric response is mathematically described by the Langevin saturation function yielding the average orientation of a single dipole in a uniform external field.<sup>7</sup> The difference between theoretical models adopting this point of view is only in the correction factor connecting the field of the charges at the capacitor plates to the local field experienced by the dipole. Historically, it was the difference in the Piekara coefficients produced by the Lorentz and Onsager local fields that was used as a strong argument in support of the Onsager theory of dipolar polarization.<sup>1</sup>

It is generally far from clear that the local, mean-field view can adequately represent the nonlinear dielectric response.<sup>8</sup> Binary dipolar correlations significantly affect even linear dielectric susceptibility through the Kirkwood correlation factor<sup>7,9</sup> and higher-order three- and four-particle correlations are required to describe the Piekara coefficient (see below). Here, a general theoretical formalism to describe the nonlinear dielectric response is

developed. The key distinction of the present formulation from the mean-field view is the recognition of many-body orientational correlations. The model allows either positive (normal) or negative (anomalous<sup>10</sup>) signs of the Piekara coefficient, as observed experimentally.<sup>3,5,10</sup> In contrast, only positive values are allowed by the mean-field theory. The formulation presented here involves two steps. We first formulate the exact equation connecting the Piekara coefficient to the fourth-order cumulant of the sample dipole moment (Sec. II). We then provide the next exact equation separating the binary dipolar correlations from the triple- and fourth-order correlations in the Piekara coefficient (Sec. III). This separation allows access to many-particle statistics and dynamics in liquids, with the potential of extracting dynamical and static length-scales not captured by the binary correlations.<sup>11,12</sup>

## II. STATIC NONLINEAR DIELECTRIC RESPONSE

The partition function of a dielectric material in the uniform field of external charges  $E_0$  is given as

$$Q(E_0) = \int e^{-\beta H_0 + \beta M E_0} d\Gamma. \quad (1)$$

In this equation,  $M$  is the total, macroscopic dipole moment of the sample in projection on the direction of the external field and  $H_0$  is the Hamiltonian of the polar liquid in the absence of the field;  $\beta = 1/(k_B T)$  is the inverse temperature. The integration is performed over the entire phase space of the liquid  $\Gamma$ .

One can consider the dipole moment  $M$  of a macroscopic sample as a stochastic variable and define the cumulant generating function<sup>13</sup>

$$e^{g(E_0)} = \langle e^{\beta M E_0} \rangle_0 = \frac{Q(E_0)}{Q(0)}, \quad (2)$$

where the angular brackets  $\langle \dots \rangle_0$  denote the statistical average in the absence of the external field. The function  $g(E_0)$  is given by the series in the field  $E_0$ , in which the

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coefficients are defined in terms of cumulants  $K_n$  of the stochastic variable  $M$

$$g(E_0) = \sum_{n=2}^{\infty} \frac{(\beta E_0)^n}{n!} K_n. \quad (3)$$

The sum starts with  $n = 2$  because the average dipole in the absence of the field is zero,  $\langle M \rangle_0 = 0$ . Since we are interested here only in the first two non-zero cumulants, we denote the second cumulant  $K_2 = \langle M^2 \rangle_0$  as the dipole moment variance  $\sigma_M^2$  and re-write the fourth cumulant  $K_4 = \langle M^4 \rangle_0 - 3K_2^2$  as  $K_4 = -3\sigma_M^4 U_N$  with

$$U_N = 1 - \langle M^4 \rangle_0 / (3\sigma_M^4). \quad (4)$$

The parameter  $U_N$  specifies the extent of deviation of the statistics of  $M$  from the Gaussian statistics;  $U_N = 0$  when  $M$  is a Gaussian stochastic variable. The subscript ‘‘N’’ specifies that certain scaling of this parameter with the number of molecules  $N$  is anticipated, in analogy to a similar parameter considered in the theory of critical phenomena.<sup>14</sup>

From Eq. (2), the average dipole moment induced by the external field is  $\langle M \rangle_E = \partial g(E_0) / \partial \beta E_0$ , where  $\langle \dots \rangle_E$  refers to the statistical average in the presence of the external field. From this relation and Eq. (3) one gets

$$\langle M \rangle_E = \sum_{n=1}^{\infty} \frac{(\beta E_0)^n}{n!} K_{n+1}. \quad (5)$$

By truncating the series after the second expansion term, one obtains for the uniform polarization of the sample

$$\frac{\langle M \rangle_E}{V} = \beta E_0 \frac{\sigma_M^2}{V} - (\beta E_0)^3 \frac{\sigma_M^4}{2V^2 \rho} B_V, \quad (6)$$

where  $\rho = N/V$  is the number density and

$$B_V = NU_N = -\frac{NK_4}{3K_2^2}. \quad (7)$$

The subscript ‘‘V’’ specifies the constant volume conditions.

The variance of the dipole moment of the bulk material scales as its volume,  $\sigma_M^2 \propto V$ . Therefore, all terms in Eq. (6) are intensive if  $B_V$  is intensive, which requires  $U_N \propto N^{-1}$ . This scaling implies that the statistics of the macroscopic dipole moment  $M$  of a thermodynamically stable phase characterized by a single free energy minimum is Gaussian ( $U_N \rightarrow 0$ ) in the thermodynamic limit  $N \rightarrow \infty$ . Only close to the critical point of transition to spontaneous polarization (ferroelectricity) can the system visit a finite number of alternative free energy minima. Transitions between these alternative configurations make the statistics of the macroscopic dipole non-Gaussian, characterized by a non-zero  $U_N$ .<sup>14</sup> On the other hand, the reduced cumulant  $B_V$  in Eq. (7) gives access to the  $O(N^{-1})$  expansion term of  $U_N$  in powers of  $N^{-1}$  and is non-zero even in the macroscopic limit, in contrast to  $U_N$  itself.

The polarization density  $\langle M \rangle_E / V$  can be related to the Maxwell field  $E$  inside the dielectric through the non-linear dielectric constant  $\epsilon_E$  depending on the field,  $\langle M \rangle_E / V = E(\epsilon_E - \epsilon_\infty) / (4\pi)$ , where  $\epsilon_\infty$  is the high-frequency dielectric constant reflecting electronic and vibrational polarizability of the dielectric.<sup>7</sup> Similarly, the linear response dielectric constant is related to the linear dielectric constant  $\epsilon_s$  as follows<sup>7</sup>

$$\frac{\beta \sigma_M^2}{V} = \frac{\Delta \epsilon_s}{4\pi} \frac{E}{E_0}, \quad (8)$$

where  $\Delta \epsilon_s = \epsilon_s - \epsilon_\infty$  and  $E_0 / E = \epsilon_s$ . Combining Eqs. (6) and (8), one can connect the excess of the nonlinear dielectric constant  $\epsilon_E$  over the linear one to the reduced cumulant  $B_V$

$$\Delta \epsilon_{E,V} = \epsilon_E - \epsilon_s = -B_V (\epsilon_s \Delta \epsilon_s)^2 \frac{\beta E^2}{8\pi \rho}. \quad (9)$$

### III. MEAN-FIELD THEORIES AND BEYOND

The standard approach to estimate the non-linear dielectric response is in terms of the mean-field model of a single dipole in an effective field of the polarized dielectric.<sup>1,10,15,16</sup> This approach results in a single-dipole Hamiltonian

$$h = h_0 - m \chi_c E, \quad (10)$$

where  $m$  is the molecular dipole moment and  $\chi_c = E_c / E$  is the ratio of the local ‘‘cavity’’<sup>17</sup> field  $E_c$  acting on dipole to the bulk Maxwell field  $E$ . In dielectric models, the definition of the cavity field comes from viewing the permanent dipole of a liquid molecule immersed in a continuum of electronically polarizable dielectric with the dielectric constant  $\epsilon_\infty$ . The molecule with its dipole cuts a spherical cavity from the surrounding dielectric with the static dielectric constant  $\epsilon_s$ . The cavity field is then calculated from the standard dielectric boundary value problem for a spherical cavity with  $\epsilon = 1$  surrounded by the dielectric with the dielectric constant  $\epsilon_s / \epsilon_\infty$ .<sup>16,18</sup> The result is

$$\chi_c = 3\epsilon_s / (2\epsilon_s + \epsilon_\infty). \quad (11)$$

The average induced dipole in the mean-field model is given by the Langevin function

$$\langle M \rangle_E = NmL(\beta m \chi_c E), \quad (12)$$

where  $L(x) = \coth(x) - 1/x$ . From this relation, one can directly obtain

$$\frac{\Delta \epsilon_{E,V}}{\epsilon_s E^2} = -\frac{3\beta}{20\pi \rho} \frac{\Delta \epsilon_s^2}{2\epsilon_s + \epsilon_\infty}. \quad (13)$$

By comparing to Eq. (9), the parameter  $B_V$  in the mean-field description becomes

$$B_V^{\text{MF}} = \frac{2\chi_c}{5\epsilon_s^2}, \quad (14)$$

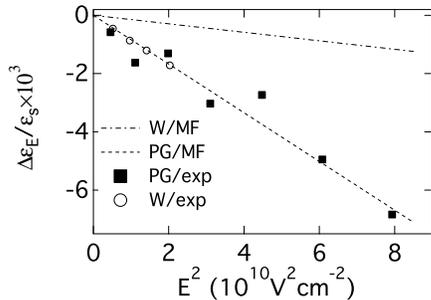


Figure 1. Relative change of the dielectric constant of propylene glycol (PG) and water (W) vs  $E^2$ . The points (exp) are laboratory measurements for PG<sup>4</sup> and water<sup>2</sup> and the lines are results of the mean-field (MF) approximation (Eq. (13)).

where the cavity field susceptibility  $\chi_c$  is given by Eq. (11).

Figure 1 shows the application of this equation to non-linear dielectric response of propylene glycol<sup>4</sup> and water.<sup>2</sup> The straight lines represent the slope predicted by Eq. (13) and the points are experimental data. The agreement with experiment is perfect for propylene glycol, but Eq. (13) underestimates the experimental slope for water. A good agreement with the mean-field approximation in the former case is most likely fortuitous (see Table I) since the quadratic in the field dielectric decrement is largely determined by the higher-order dipolar correlations absent in the mean-field theory as we discuss next.

Assume that the external field of the dielectric experiment is along the  $z$ -axis of the laboratory frame. The fourth-order cumulant of the sample dipole moment can then be re-written as a sequence of terms of increasing correlation order

$$m^{-4}\langle M_z^4 \rangle_0 = \frac{N}{5} + \sum_{i \neq j} [3\langle e_{iz}^2 e_{jz}^2 \rangle_0 + 4\langle e_{iz} e_{jz}^3 \rangle_0] \quad (15)$$

$$+ 6 \sum_{i \neq j \neq k} \langle e_{iz} e_{jz} e_{kz}^2 \rangle_0 \quad (16)$$

$$+ \sum_{i \neq j \neq k \neq m} \langle e_{iz} e_{jz} e_{kz} e_{mz} \rangle_0. \quad (17)$$

Here,  $e_{iz}$  is the  $z$ -projection of the unit vector of the molecular dipole. The two-particle correlations can be expressed in terms of the  $k = 0$  values of the Fourier transformed pair distribution functions

$$3\langle e_{iz}^2 e_{jz}^2 \rangle_0 = N^2/3 + (N/3)\rho \tilde{h}^0(0), \quad (18)$$

$$4\langle e_{iz} e_{jz}^3 \rangle_0 = (4N/15)\rho \tilde{h}^\Delta(0).$$

In this equation,  $h^0(r) = g^0(r) - 1$  is the angular isotropic pair correlation function of the liquid and  $\tilde{h}^0(k)$  is its Fourier transform. Further,  $h^\Delta(r)$  is the projection of the two-particle correlation function, depending on the orientations of two molecules, on the rotational invariant of the scalar product of the corresponding dipolar unit vectors,  $\Delta(12) = \hat{\mathbf{e}}_1 \cdot \hat{\mathbf{e}}_2$ ;  $\tilde{h}^\Delta(k)$  is the corresponding Fourier transform.<sup>19</sup> The  $k = 0$  values of these two

correlation functions are expressed in terms of the liquid isothermal compressibility  $\chi_T$  and the Kirkwood factor  $g_K$ .<sup>20</sup> From this connection, one can re-write the fourth-order cumulant of the dipole moment as

$$\frac{K_4}{m^4} = -\frac{2N}{15} \left[ 1 - \frac{5}{2}\beta^{-1}\rho\chi_T - 6(g_K - 1) - H_3 - H_4 \right], \quad (19)$$

where  $H_3$  and  $H_4$  represent the three- and four-particle orientational correlations, respectively. Specifically one gets for these terms

$$H_3 = \frac{45}{N} \sum_{i \neq j \neq k} \langle e_{iz} e_{jz} e_{kz}^2 \rangle_0 - 5N(g_K - 1),$$

$$H_4 = \frac{15}{2N} \sum_{i \neq j \neq k \neq m} \langle e_{iz} e_{jz} e_{kz} e_{mz} \rangle_0 - \frac{5N}{2}(g_K - 1)^2. \quad (20)$$

Here, we have used the relation  $g_K = 3\langle M_z^2 \rangle_0 / (m^2 N)$ . We also stress that the average  $\langle \dots \rangle_0$  is over configurations of the liquid in the absence of external field.  $H_3$  and  $H_4$ , therefore, describe triple and four-particle correlations of dipolar orientations in the unperturbed liquid.

The triple correlations can be estimated by applying the Kirkwood superposition approximation (KSA)<sup>19</sup> for the three-particle distribution function

$$g(\mathbf{r}_1\omega_1, \mathbf{r}_2\omega_2, \mathbf{r}_3\omega_3) = g(\mathbf{r}_{12}\omega_1\omega_2)g(\mathbf{r}_{13}\omega_1\omega_3)g(\mathbf{r}_{23}\omega_2\omega_3), \quad (21)$$

where  $\mathbf{r}_i$  and  $\omega_i$  are the positions and orientations of three different particles in the liquid;  $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$ . The result of applying the KSA is

$$H_3^{\text{KSA}} = 9(g_K - 1)^2. \quad (22)$$

However, we have found that the KSA significantly overestimates  $H_3$  when tested against Monte Carlo simulations of dipolar hard sphere fluids (see Supplementary Materials<sup>21</sup> (SM)). The values of  $H_3$  from simulations also show a significant dependence on the system size (Table S1 in SM) and therefore are not analyzed here. Overall, neither theory nor simulations provide reliable estimates of the  $H_3$  and  $H_4$  terms in Eqs. (19) and (20). They need to be accessed from experiment.

Leaving  $H_3$  and  $H_4$  as unspecified parameters, the reduced cumulant  $B_V$  describing the nonlinear dielectric increment (Eq. (9)) is given as the sum of binary,  $B^{(2)}$ , and higher-order,  $B^{(3,4)}$ , correlation components

$$B_V = B^{(2)} + B^{(3,4)}. \quad (23)$$

They are given by the following relations

$$B^{(2)} = \frac{6}{5g_K^2} \left[ 1 - \frac{5}{2}\beta^{-1}\rho\chi_T - 6(g_K - 1) \right], \quad (24)$$

$$B^{(3,4)} = -\frac{6}{5g_K^2} [H_3 + H_4].$$

Table I. Reduced cumulant  $B_V \times 10^3$  calculated in the mean-field approximation (Eq. (14)) and estimated from experimental Piekara coefficients.<sup>3</sup> Also listed are binary  $B^{(2)}$  components of  $B_V$  calculated from experimental parameters according to Eq. (24). The Kirkwood correlation parameter  $g_K$  in this equation was calculated from Wertheim's 1-RPT theory<sup>26</sup> of polarizable liquids (see SM<sup>21</sup>). These calculations are compared in the last column ( $g_K^O$ ) with estimates based on the Onsager relation.<sup>7</sup> All reduced cumulants listed in the table are multiplied by  $10^3$ . The parameters for the solvents listed here are taken from the database of solvent properties in Ref. 22.

Liquid	$B_V^{\text{MF}}$	$B_P^{\text{exp}}$	$B^{(2)}$	$g_K$	$g_K^O$
Water	0.1	0.9	-1554	2.61	2.87
Methanol	0.5	8.9	-1568	2.54	3.09
Ethanol	1.0	12.4	-1523	2.74	3.12
Bromobenzene	16.8	-13.7	9661	0.63	0.66
Iodobenzene	21.9	-58.4	7356	0.68	0.46

From Eqs. (23) and (24), the sign of the reduced cumulant  $B_V$  might alter depending on the relative magnitudes of  $B^{(2)}$  and  $B^{(3,4)}$ . Both positive and negative values of the Piekara coefficient have been recorded experimentally<sup>3,5</sup> (Table I), but only a positive value  $B_V^{\text{MF}} > 0$  is predicted by the mean-field theory (Eq. (14)). The compressibility component in Eq. (23) typically amounts to  $\beta^{-1}\rho\chi_T \simeq 0.05 - 0.1$  for polar molecular liquids<sup>22</sup> and is not expected to make  $B_V$  negative. However, the Kirkwood correlation parameter  $g_K$  can be significantly greater than unity ( $g_K \simeq 2.2$  in liquid water<sup>23</sup> and 2.4 in ice<sup>24</sup>). Consequently,  $B^{(2)}$  in Eq. (23) can become negative for liquids with strong alignment of neighboring dipoles. The overall sign of  $B_V$  is still hard to predict theoretically without knowledge of both terms in Eq. (23). Equations (23) and (24), which are exact for the dipolar polarization of the liquid, in fact provide an experimental access to non-trivial higher order dipolar correlations, which are currently hard to estimate theoretically. We also note that, since the Kirkwood parameter is typically a weak function of temperature<sup>25</sup> (with notable exceptions<sup>5</sup>), both the mean-field result in Eq. (13) and the exact expression in Eq. (9) predict an inverse temperature scaling,  $\propto T^{-1}$ , of the Piekara coefficient, in contrast to the often anticipated  $\propto T^{-3}$  scaling.<sup>2,16</sup>

#### IV. MEASUREMENTS AT CONSTANT PRESSURE

Dielectric experiment measures the free energy of charging the plane capacitor, which is connected to the dielectric constant through the corresponding capacitance. The data are typically collected at constant pressure, while theoretical calculations performed here refer to the constant volume (density). This distinction does not appear in the linear response since the average interaction of the dipole with the external field integrates to zero when the unperturbed uniform density  $\rho(1) = \rho$  is

assumed in the statistical averages,  $\int \rho(1)\mathbf{m}_1 \cdot \mathbf{E}_0 d\omega_1 = 0$ ;  $\rho(1)$  is the one-particle distribution function. This integral becomes non-zero and starts to depend on the ensemble in high fields when  $\rho(1) \neq \rho$ ,<sup>8</sup> which requires corrections to connect properties measured at different conditions.

The transition to the constant pressure conditions requires correction for electrostriction, i.e., change of the liquid density (either compression or decompression<sup>27</sup>) in the external electric field. Following the arguments presented by Frank,<sup>27</sup> one gets for the alteration of the dielectric constant in the electric field

$$\Delta\epsilon_{E,P} = \Delta\epsilon_{E,V} + \chi_T(\epsilon_s - 1)^2 \frac{E^2}{8\pi} \left( \frac{\partial \ln \epsilon_s}{\partial \ln \rho} - 1 \right)^2, \quad (25)$$

where  $\Delta\epsilon_{E,V}$  is given by Eq. (9) (note a typo in Eq. (51) in Ref. 27 which contains an extra (1/2) factor). The logarithmic derivative of the dielectric constant over the density can be calculated from the Wertheim-type<sup>26</sup> expressions for the dielectric constant of dipolar-polarizable liquids<sup>9</sup> by neglecting the density dependence of the Kirkwood factor. The result is (see SM<sup>21</sup>)

$$\frac{\partial \ln \epsilon_s}{\partial \ln \rho} = \frac{(\epsilon_s - 1)(2\epsilon_s + 1)}{2\epsilon_s^2 + 1}. \quad (26)$$

One finally gets a relation between the reduced cumulant  $B_P$  at constant pressure and  $B_V$  at constant volume

$$B_V = B_P + \beta^{-1}\rho\chi_T \left( \frac{(\epsilon_s - 1)(\epsilon_s + 2)}{\epsilon_s\Delta\epsilon_s(2\epsilon_s^2 + 1)} \right)^2. \quad (27)$$

For the data shown in Table I the distinction between  $B_P^{\text{exp}}$  and  $B_V^{\text{exp}}$  is insignificant and only  $B_P^{\text{exp}}$  is listed.

Similar arguments yield the correction to the reduced cumulant measured at the conditions of the constant chemical potential, when the liquid subjected to the field is kept in equilibrium with the same liquid in zero field. One gets in this case

$$B_\mu = B_V + \beta^{-1}\rho\chi_T \frac{(\epsilon_s - 1)^3(2\epsilon_s + 1)(\epsilon_s + 2)}{[\epsilon_s\Delta\epsilon_s(2\epsilon_s^2 + 1)]^2}. \quad (28)$$

The experimental data shown in Table I allow for an estimate of relative weights of binary and higher-order correlations in the reduced cumulant  $B_{V,P}$ . The binary components  $B^{(2)}$  based on experimental compressibilities<sup>22</sup> and calculated Kirkwood factors are listed in Table I. The Kirkwood factors were calculated from Wertheim's 1-RPT theory<sup>26</sup> of polar-polarizable liquids (see SM<sup>21</sup>). The next level of the theory renormalization, known as 2-RPT, is less consistent with simulations than the 1-RPT theory<sup>28</sup> and, therefore, the latter was used in the calculations.

The values of the binary components  $B^{(2)}$  are very high, indicating a strong compensation between the binary and higher-order correlations in the reported Piekara coefficients. These results suggest that higher-order correlations are significant and cannot be neglected.

This finding also implies that mean-field theories have no physical reason to be successful for this problem. Correlations of all orders are significant, in contrast to the requirement of negligible correlations implicit to the success of mean-field models.

## V. CONCLUSIONS

Equations (23) and (24) are the main result of this study. They achieve the separation of the reduced cumulant  $B_V$  into the “trivial” binary density and dipolar correlations,  $B^{(2)}$ , and less trivial, and harder to calculate, three- and four-particle orientational correlations,  $B^{(3,4)}$ . The binary term is given in terms of the  $k = 0$  density (compressibility) and orientational (Kirkwood factor) structure factors of the liquid. Equations (23) and (24), which are exact, provide experimental access to non-trivial higher-order orientational correlations through dielectric high-field measurements. These many-particle correlations are sensitive to the thermodynamic state of the liquid<sup>29</sup> and can gauge the increase of the correlation/cooperativity length on approach to the glass transition.<sup>11,12</sup> It is hard in this regard to escape the connection between the reduced cumulant  $B_{V,P}$  considered here and a similar parameter used to monitor the transition to quenched disorder in spin glasses.<sup>14</sup> The component  $B^{(3,4)}$  should be also sensitive to the formation of highly correlated topological structures in liquids, such as rings and chains,<sup>5</sup> and might help to identify their emergence.

The present results differ significantly from the predictions of the mean-field theory. The latter assigns the non-linear dielectric increment to the orientational saturation of each single dipole in the liquid. Only a decrement of the dielectric constant and  $B_V^{\text{MF}} > 0$  are allowed in this framework. In contrast, Eqs. (23) and (24) stress the significance of multi-particle dipolar correlations and allow  $B_V$ , and the Piekara coefficient, to be either positive or negative.

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## REFERENCES

- <sup>1</sup>J. H. van Vleck, *J. Chem. Phys.* **5**, 556 (1937).
- <sup>2</sup>A. E. Davies, M. J. van der Sluijs, G. P. Jones, and M. Davies, *J. Chem. Soc., Faraday Trans. 2: Molecular and Chemical Physics* **74**, 571 (1978).
- <sup>3</sup>M. Dutkiewicz and E. Dutkiewicz, *J. Soln. Chem.* **22**, 787 (1993).
- <sup>4</sup>S. Weinstein and R. Richert, *Phys. Rev. B* **75**, 064302 (2007).
- <sup>5</sup>L. P. Singh and R. Richert, *Phys. Rev. Lett.* **109**, 167802 (2012).
- <sup>6</sup>S. Samanta and R. Richert, *J. Chem. Phys.* **142**, 044504 (2015).
- <sup>7</sup>C. J. F. Böttcher, *Theory of Electric Polarization*, Vol. 1 (Elsevier, Amsterdam, 1973).
- <sup>8</sup>J. D. Ramshaw, *J. Chem. Phys.* **73**, 5294 (1980).
- <sup>9</sup>G. Stell, G. N. Patey, and J. S. Høye, *Adv. Chem. Phys.* **48**, 183 (1981).
- <sup>10</sup>J. Liszi, *J. Chem. Phys.* **74**, 6896 (1981).
- <sup>11</sup>J.-P. Bouchaud and G. Biroli, *Phys. Rev. B* **72**, 064204 (2005).
- <sup>12</sup>C. Crauste-Thibierge, C. Brun, F. Ladieu, D. L’Hôte, G. Biroli, and J. P. Bouchaud, *Phys. Rev. Lett.* **104**, 165703 (2010).
- <sup>13</sup>C. W. Gardiner, *Handbook of Stochastic Methods* (Springer, Berlin, 1997).
- <sup>14</sup>D. P. Landau and K. Binder, *Monte Carlo simulations in statistical physics* (Cambridge University Press, Cambridge, 2000).
- <sup>15</sup>A. K. Jha and K. F. Freed, *J. Chem. Phys.* **128**, 034501 (2008).
- <sup>16</sup>R. L. Fulton, *J. Chem. Phys.* **130**, 204503 (2009).
- <sup>17</sup>L. Onsager, *J. Am. Chem. Soc.* **58**, 1486 (1936).
- <sup>18</sup>J. D. Jackson, *Classical Electrodynamics* (Wiley, New York, 1999).
- <sup>19</sup>C. G. Gray and K. E. Gubbins, *Theory of Molecular Liquids* (Clarendon Press, Oxford, 1984).
- <sup>20</sup>J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic Press, Amsterdam, 2003).
- <sup>21</sup>See supplementary material at [URL will be inserted by AIP] for details of the simulation protocol.
- <sup>22</sup>R. Schmid and D. V. Matyushov, *J. Phys. Chem.* **99**, 2393 (1995).
- <sup>23</sup>M. Sharma, R. Resta, and R. Car, *Phys. Rev. Lett.* **98**, 247401 (2007).
- <sup>24</sup>N. Bonnet and N. Marzari, *Phys. Rev. Lett.* **113**, 245501 (2014).
- <sup>25</sup>J. Jadżyn and J. Świergiel, *Phys. Chem. Chem. Phys.* **14**, 3170 (2012).
- <sup>26</sup>M. S. Wertheim, *Mol. Phys.* **37**, 83 (1979).
- <sup>27</sup>H. S. Frank, *J. Chem. Phys.* **23**, 2023 (1955).
- <sup>28</sup>S. Gupta and D. V. Matyushov, *J. Phys. Chem. A* **108**, 2087 (2004).
- <sup>29</sup>G. S. Rushbrooke, in *Physics of Simple Liquids*, edited by H. N. V. Temperley, J. S. Rowlinson, and G. S. Rushbrooke (Wiley, 1968) pp. 25–58.