

Temperature derivative of the dielectric constant gives access to multipoint correlations in polar liquids

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Fluctuations of the dipole moment of a macroscopic dielectric sample are induced by thermal motions. The variance of the sample dipole moment, characterizing the extent of thermal fluctuations, is a decaying function of temperature for many polar liquids. This result is inconsistent with the Nyquist (fluctuation-dissipation) theorem predicting the variance of a macroscopic property to grow linearly with temperature. The reason for a qualitatively different behavior is in strong multi-particle correlations of dipolar orientations. An equation connecting the temperature slope of the dielectric constant to a static three-point correlation function is derived. When applied to experimental data for polar and hydrogen-bonding liquids at normal conditions, the three-point correlations of different liquids fall on a single master curve as a function of the dielectric constant. Static three-point correlation functions can potentially reflect the growing spatial correlation length on approach to the glass transition. However, the measured temperature slope of the dielectric constant of glycerol does not indicate a change in such a lengthscale.

I. INTRODUCTION

When one considers thermal fluctuations of macroscopic properties near equilibrium, the first point of departure is the Nyquist theorem¹ suggesting that the variance of a macroscopic extensive variable A is proportional to the number of particles in the system N and temperature T : $\langle(\delta A)^2\rangle \propto NT$, $\delta A = A - \langle A \rangle$. This statement is the static limit of the fluctuation-dissipation theorem connecting the variance produced by intrinsic thermal fluctuations to susceptibility $\chi_A(T)$ in response to a small perturbation:² $\langle(\delta A)^2\rangle = NT\chi_A(T)$. The Nyquist theorem thus corresponds to a temperature-independent susceptibility $\partial\chi_A/\partial T = 0$.

There are notable deviations from the expectations of the Nyquist theorem ranging from nano-electronics³ to enzyme kinetics.⁴ Current fluctuations, for which the Nyquist theorem was formulated, are composed of collective plasmon modes and random incoherent quasiparticle excitations.³ The long-wavelength limit of the collective plasmon structure factor $\langle|\rho(k)|^2\rangle \propto Nk^2\omega_p^{-1}$ (ω_p is the plasmon frequency) does not follow the Nyquist prediction. One can, therefore, anticipate that collective dipolar excitations of polar liquids, driven by long-range dipolar correlations,^{5,6} is another such case.

Figure 1 shows the variance $\langle\mathbf{M}^2\rangle$ of the dipole moment \mathbf{M} of a macroscopic sample of glycerol vs T . The variance $\langle\mathbf{M}^2\rangle$ was calculated from the dielectric constant of glycerol $\epsilon(T)$, obtained experimentally in this study (see supplementary material⁷), and its volume $V(T)$ ^{8,9} according to the exact Kirkwood-Onsager equation⁶

$$\frac{(\epsilon - 1)(2\epsilon + 1)}{\epsilon} = \frac{4\pi\beta}{V}\langle\mathbf{M}^2\rangle. \quad (1)$$

Here, $\beta = 1/(k_B T)$, $\langle\mathbf{M}\rangle = 0$, and the brackets $\langle\dots\rangle$ denote the statistical average in the absence of the external electric field. The dipole moment in this equation includes both the permanent and induced dipoles. A number of formulations have been proposed,^{6,10} starting from the Onsager dielectric formula,¹¹ separating permanent and induced dipoles in \mathbf{M} . Here, this separation is not sought and the entire dipole moment of the liquid is considered.

Figure 1 clearly shows that $\langle\mathbf{M}^2\rangle$ dramatically violates the prescription of the Nyquist theorem: it decreases with increasing temperature, instead of the predicted increase. If the Nyquist theorem was valid for polar liquids, $\beta\langle\mathbf{M}^2\rangle$ would be temperature independent, implying the dielectric constant depending on temperature only through $V(T)$. This prediction is inconsistent with observations.

In contrast to the dipole moment, thermal fluctuations of the liquid density behave more in accord with the Nyquist theorem (Fig. 1). The $k = 0$ value of the density-density structure factor

$$S(0) = \langle(\delta N)^2\rangle/\langle N \rangle = k_B T \rho \beta_T \quad (2)$$

describes fluctuations $\delta N = N - \langle N \rangle$ of the number of particles N in a given volume V relative to the average value $\langle N \rangle$. Further, in Eq. (2), $\rho = \langle N \rangle/V$ is the number density and $\beta_T(T)$ is the isothermal compressibility of the liquid. The latter property was taken from direct measurements¹² and compared to the use of adiabatic compressibility $\beta_S(T)$ from Brillouin scattering^{13,14} to obtain $S(0)$ in Fig. 1 [$\beta_T/\beta_S = C_P/C_V > 1$ ¹⁵].

The variance of the dipole moment can be related to the scalar trace of the longitudinal (L) and transverse (T) components of the dipolar structure factors⁵ at $k = 0$

$$[m^2\langle N \rangle]^{-1}\langle\mathbf{M}^2\rangle = \frac{1}{3}(S^L(0) + 2S^T(0)). \quad (3)$$

Therefore, Eqs. (2) and (3) carry similar physical meaning. However, the difference in the range of correlations

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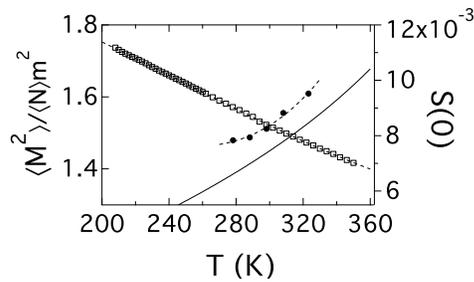


Figure 1. The variance of the dipole moment of glycerol $\langle \mathbf{M}^2 \rangle / \langle N \rangle m^2$ vs temperature, where $m = 4.6$ D is the dipole moment of the glycerol molecule. The points are calculated from experimental $\epsilon(T)$ (this study) and $V(T)$ ^{8,9} at constant pressure according to Eq. (1). The solid line referring to the right axis shows $S(0)$ [Eq. (2)] calculated from the adiabatic bulk modulus of glycerol supplied by Brillouin scattering.^{13,14} The closed points refer to direct measurements of the isothermal compressibility of glycerol.¹² The dashed lines are polynomial fits through the experimental points to guide the eye.

implicit to the density and polarization collective variables is responsible for qualitatively different temperature variations of their corresponding structure factors.

The Nyquist theorem is an empirical observation, which does not have to be satisfied in all cases. It can be rationalized by some simple models. For instance, if fluctuations of the condensed medium can be represented by an ensemble of classical harmonic oscillators, any macroscopic quantity A , which can be extended into a linear combination of oscillators' displacements, will show the behavior consistent with the Nyquist theorem. The density structure factor in Fig. 1 shows this expected behavior since one can think of density fluctuations in a dense material as a superposition of cage rattling displacements of individual molecules. These displacements are correlated at high densities, and the Nyquist theorem does not hold exactly. The predicted linear scaling with temperature can be violated even for individual oscillators.^{16,17} An example is the dynamical transition in proteins recorded by the temperature-dependent displacement of a single iron atom of the protein.¹⁷ The linear scaling is observed for low- and high-temperature displacements, but the break in the slope signals the point of dynamical transition.

The approximation of many independent displacements breaks down for the macroscopic dipole moment of the sample (as well as for plasmonic collective excitations mentioned above), even though individual molecular rotations can be thought of as harmonic librations. The obvious difficulty with the orientational dipolar degrees of freedom is their strong, many-particle correlations.¹⁸ The goal of this article is to understand the microscopic origin of the peculiar temperature dependence of the dipole moment variance, which appears to be quite general for polar liquids. We show below that indeed the temperature slope of $\langle \mathbf{M}^2 \rangle$ is defined by three- and four-particle correlations between molecular dipoles.

It is clear from Eq. (1) that the temperature depen-

dence of $\langle \mathbf{M}^2 \rangle$ is fully determined by the dielectric function $\epsilon(T)$. Temperature slopes of $\epsilon(T)$ span a relatively narrow range among common polar liquids¹⁹ and one can anticipate that the results discussed here for glycerol represent general trends applicable to many polar liquids.

The temperature derivative of the dielectric constant is related to a broad class of multipoint correlation functions obtained from the temperature derivative of the two-point correlation function $C(\mathbf{r}, t) = \langle \delta a(\mathbf{r}, t) \delta a(\mathbf{0}, 0) \rangle$, where $a(\mathbf{r}, t)$ is an intensive variable, which should be equated with the polarization density $P_z(\mathbf{r}, t)$ along the field for the dielectric response.²⁰ The temperature derivative of $C(\mathbf{r}, t)$ produces three point correlation functions involving the fluctuation of the system energy $\delta H(t)$: $\chi_T(\mathbf{r}, t) \propto \langle \delta a(\mathbf{r}, t) \delta a(\mathbf{0}, 0) \delta H(0) \rangle$. These correlation functions,²¹ and related to them four-point correlation functions,²⁰ are believed to reflect growing spatial correlations in supercooled liquids close to the laboratory glass transition.

As we show below, $(\partial \epsilon / \partial T)_V$ gives direct access to the static limit of three point correlation functions. Given that dynamic fragility is matched by fragility indicators based on purely thermodynamic (steady state) properties of glass-formers,^{20,22,23} one can expect that static correlations must be sufficient to detect the appearance of long-range correlated domains anticipated to affect the dynamics on approach to the laboratory glass transition.^{16,24} If such a possibility can be realized, the temperature slope of the dielectric constant is a good property to study. The reason is that, as we show below, this parameter is strongly affected by multi-body correlations not shadowed by more trivial binary correlations, as is the case for density fluctuations and the corresponding compressibility.

II. DERIVATION

The starting point of the derivation is the Maxwell relation connecting the liquid entropy S with the polarization density P created by the field of external charges. In order to be more specific, we consider the dielectric material placed in the plane capacitor with the density of charge carriers at the metal plates σ_0 . The charge at the plates creates the electric field of external charges $E_0 = 4\pi\sigma_0$. Because of the planar slab geometry of the dielectric sample, the electric induction D is equal to the external field, $D = E_0$.²⁵ When the external charges and temperature are varied at constant volume, the variation of the system free energy is

$$\delta F_V = -S\delta T + (V/4\pi)E\delta E_0, \quad (4)$$

where E is the macroscopic field within the dielectric (Maxwell field). One can then write the Maxwell relation connecting the alteration of the entropy due to the change in charge on the plates to the temperature variation of

the polarization density,^{10,25} $(dE)_{E_0} = -4\pi(dP)_{E_0}$,

$$\left(\frac{\partial S}{\partial E_0}\right)_{VT} = V \left(\frac{\partial P}{\partial T}\right)_{VE_0}. \quad (5)$$

The left-hand side of Eq. (5) directly relates to the temperature derivative of the dielectric constant [Eq. (10.18) in Ref. 25]

$$\left(\frac{\partial S}{\partial E_0}\right)_{VT} = \frac{VE_0}{4\pi\epsilon^2} \left(\frac{\partial \epsilon}{\partial T}\right)_V. \quad (6)$$

One therefore obtains the constant-volume temperature derivative of the dielectric constant

$$\left(\frac{\partial \epsilon}{\partial T}\right)_V = \frac{4\pi\epsilon^2}{E_0} \left(\frac{\partial P}{\partial T}\right)_{VE_0}. \quad (7)$$

The temperature derivative of the average polarization of the sample P can be calculated from general expressions of statistical mechanics of a polar liquid characterized by the Hamiltonian H_0 and perturbed by the external field with the perturbation Hamiltonian $H' = -M_z E_0$, where the external field is along the z -axis of the laboratory frame. Here, M_z is the fluctuating dipole moment of the dielectric sample and $\langle M_z \rangle_E = PV$; $\langle \dots \rangle_E$ is the statistical average in the presence of the external field, in contrast to $\langle \dots \rangle$ denoting the average in the absence of the field. Performing the perturbation expansion of P in H' and keeping only the terms linear in E_0 , one obtains (see supplementary material for more detail⁷)

$$T \left(\frac{\partial \epsilon}{\partial T}\right)_V = \frac{4\pi\beta\epsilon^2}{V} [\beta \langle M_z^2 \delta H_0 \rangle - \langle M_z^2 \rangle], \quad (8)$$

where, as above, $\langle M_z \rangle = 0$ and $\delta H_0 = H_0 - \langle H_0 \rangle$. With the account for the usual perturbation result¹⁰ $(\beta/V) \langle M_z^2 \rangle = (\epsilon - 1)/(4\pi\epsilon)$ one arrives at the final equation

$$\left(\frac{\partial \ln \epsilon}{\partial \ln T}\right)_V = 1 + \epsilon(M_T - 1). \quad (9)$$

In Eq. (9),

$$M_T = (4\pi\beta^2/V) \langle M_z^2 \delta H_0 \rangle \quad (10)$$

is a three-point correlation function, which incorporates three- and four-particle orientational correlations of the molecular dipoles. This is easy to see by separating H_0 into the sum of isotropic, $H_0'(\mathbf{r})$, and anisotropic, $H_0''(\mathbf{r}, \boldsymbol{\omega})$, intermolecular interactions. The fluctuations of the isotropic interactions $\delta H_0'$ decouple from M_z^2 in the orientational angular variables of the molecules $\boldsymbol{\omega}$. They therefore produce zero contribution to M_T by virtue of $\langle \delta H_0' \rangle = 0$. It is only $\delta H_0''$ that will statistically couple to M_z^2 and produce a non-vanishing M_T .

If dipole-dipole interactions dominate the orientational part of the interaction potential in H_0 , they can be written as $\mathbf{m}_j \cdot \mathbf{T}_{jk} \cdot \mathbf{m}_k$. Here, distinct ($j \neq k$) molecular dipole moments \mathbf{m}_j and \mathbf{m}_k are contracted with the

dipolar tensor \mathbf{T}_{jk} . From this interaction potential, the correlation function M_T includes the terms of the form

$$\sum_{i,j \neq k,\ell} \langle m_{iz} \mathbf{m}_j \cdot \mathbf{T}_{jk} \cdot \mathbf{m}_k m_{\ell z} \rangle. \quad (11)$$

The parts of the sum with $i = \ell$ will produce three-particle correlations, while all other terms with $i \neq \ell$ will result in four-particle dipolar correlations.

Also notice that M_T in Eq. (10), involving the product of three extensive variables, is distinct from three point correlators constructed based on the time correlation functions of an intensive spatial field.²⁰ This is easy to see by contrasting Eq. (10) with $\chi_T(t) \propto \int \langle P_z(\mathbf{r}, 0) P_z(\mathbf{r}, t) \delta H_0 \rangle d\mathbf{r}$, where $P_z(\mathbf{r}, t) = \sum_j m_{zj} \delta(\mathbf{r} - \mathbf{r}_j(t))$. It is clear that $\chi_T(0) = 0$, while the static correlation function M_T , based on extensive variables, is non-zero. It is important to stress that $\chi_T(t)$ defined from intensive polarization density in Ref. 20 is not accessible by dielectric spectroscopy. Our definition of the three-point correlation function carries the correct form and is consistent with the one adopted in Ref. 26.

Equation (9) shows that the temperature slope $\epsilon(T)$ is directly affected by multi-particle dipolar correlations. This observation explains the puzzling result in Fig. 1: an ensemble of librating dipoles, strongly affected by multi-body correlations, does not follow the recipe derived for nearly independent harmonic oscillators (Nyquist theorem). The negative slope of the dielectric constant usually observed for molecular liquids can be obtained even at $M_T = 0$. However, this result would imply a substantial increase of the slope magnitude with increasing ϵ , which is not typically observed. In order to be consistent with observed $\epsilon(T)$ one has to require $M_T < 1$. It is also reasonable to anticipate $M_T > 0$ since increasing the energy of the system, $\delta H_0 > 0$, should lead to a higher variance of the dipole moment [Eq. (10)]. With the condition $0 < M_T < 1$, a strong increase of the slope magnitude in Eq. (9) is avoided when M_T as a function of ϵ asymptotically approaches unity from below. This is indeed a general result obtained from analyzing experimental data as we show next.

III. EXPERIMENTAL DATA

The temperature derivative of the dielectric constant at constant volume required in Eq. (9) is usually not reported, but can be extracted from combined measurements of the temperature dependence at constant pressure and the pressure dependence at constant temperature. The thermodynamic route to the desired relation is

$$\left(\frac{\partial \epsilon}{\partial T}\right)_V = \left(\frac{\partial \epsilon}{\partial T}\right)_P + \frac{\alpha_P}{\beta_T} \left(\frac{\partial \epsilon}{\partial P}\right)_T, \quad (12)$$

where α_P is the isobaric expansivity. The experimental data for the temperature and pressure slopes of $\epsilon(T, P)$

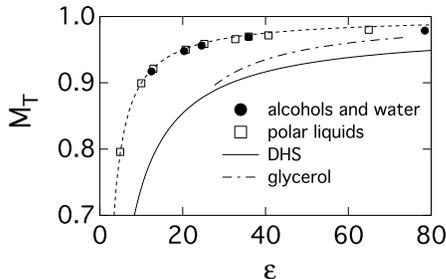


Figure 2. M_T calculated from Eqs. (9) and (12) for polar liquids (open points) and alcohols and water (closed points) at $T = 298$ K. The experimental data are taken from Ref. 19 and the dashed line is the fit to $M_T = 1 - \epsilon^{-1} - a\epsilon^{-2}$ with $a = 0.038$. The solid line indicates M_T from numerical simulations of fluids of dipolar hard spheres (DHSs) at the reduced density $\rho\sigma^3 = 0.8$, σ is the hard-sphere diameter.²⁷ The dash-dotted line is obtained from $(\partial\epsilon/\partial T)_P$ of glycerol, used instead of $(\partial\epsilon/\partial T)_V$ in Eq. (9) (higher dielectric constants correspond to lower temperatures).

compiled in Ref. 19 for a number of molecular liquids are used in Fig. 2 to extract the parameter M_T (the list of liquids used in the analysis is given in supplementary material⁷). We note that the second summand in Eq. (12) typically reduces the magnitude of the constant-pressure slope of the dielectric constant by about 20%.

The experimental data obtained at $T = 298$ K for a number of polar and hydrogen-bonding (alcohols and water) liquids all fall on one master curve $M_T(\epsilon)$ suggesting that M_T approaches unity from below with increasing ϵ thus keeping the temperature slope of $\epsilon(T)$ negative and relatively constant in magnitude. The fit of the experimental data suggests an empirical relation $(\partial\epsilon/\partial T)_V = -a(T)/T$. Since no data exist on the dependence $a(T)$, no further conclusions can be made at this point.

Experimental results are compared in Fig. 2 to Monte Carlo simulations of fluids of dipolar hard spheres (solid line).²⁷ For these liquids held at constant density the dielectric constant $\epsilon(y)$ is a function of a single parameter of the effective density of dipoles in the liquid⁶ $y = (4\pi/9)\beta\rho m^2$, m is the molecular dipole. Therefore, one gets $(\partial\epsilon/\partial T)_V = -(y/T)(\partial\epsilon/\partial y)_\rho$. Fitting functions for $\epsilon(y)$ from simulations²⁷ were used to produce $M_T(\epsilon)$ in Fig. 2. These results suggest that the liquid of dipolar hard spheres show a stronger temperature dependence of its dielectric constant compared to typical molecular liquids, which might be related to a denser packing of molecular liquids at standard conditions. Along similar lines, the dielectric constant of an ideal gas of dipolar particles satisfies the relation $\epsilon(y) = (1 - 3y)^{-1}$. When substituted to Eq. (9), it results in $M_T = 0$, as expected for an ensemble of non-interacting particles.

We have also provided $M_T(\epsilon)$ for glycerol in Fig. 2 (dash-dotted line). This calculation involves the temperature derivative of the dielectric constant at constant pressure. This implies that the second summand in Eq.

(12) was not included and the result is not as accurate as the calculations done for liquids at standard conditions. It provides, however, an estimate of the variation of M_T for a single glass-forming liquid on approach to the point of laboratory glass transition (the higher end on the dielectric constant scale).

IV. CONCLUSIONS

We have shown here that the peculiar temperature dependence of the variance of the dipole moment of a polar liquid has its origin in the three-point static correlation function, which accommodates three- and four-dipole microscopic correlations in the liquid. This correlation function can be extracted from experimental data and turns into a universal curve as a function of the dielectric constant at isothermal conditions. It approaches unity from below thus establishing a negative slope of $\epsilon(T)$.

The experimental data analyzed here are clearly insufficient to make conclusions regarding growing spatial correlations in low-temperature liquids. The anticipated growth of the correlation length in super-cooled liquids has been recently connected to three-point time correlation functions $\chi_T(t)$ obtained from the temperature derivative of the two-point time correlation function.²⁰ Given that the dynamic and thermodynamic fragility can be matched to each other,²³ one can anticipate that static three-point correlation functions $\chi_T(0)$ should also reflect the length of spatial correlations. In the present analysis, $\chi_T(0)$ is directly related to the temperature slope of $\epsilon(T)$. Therefore, any changes in the correlation length on approach to the glass transition should be reflected by the alteration of the dielectric constant slope. No such changes are found for glycerol. The dash-dotted line in Fig. 2 represents the three-point correlation function $M_T(\epsilon)$ calculated from glycerol's $\epsilon(T)$. It is consistent with calculations done for room-temperature polar liquids and actually slows down in its variation when approaching the glass transition.²⁸

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- ²⁸Note that the four-point time correlation function is given as $\chi_4(t) \propto T^2 \chi_T(t)$ (Ref. 20). From Fig. 2, $\chi_4(0)$ decreases when the temperature is lowered toward the glass transition temperature.