Debye-Waller Factor of Liquid Silica: Theory and Simulation

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We show that the prediction of mode-coupling theory for a model of a network-forming strong glass former correctly describes the wave-vector dependence of the Debye-Waller factor. To obtain a good description it is important to take into account the triplet correlation function c_3, which we evaluate from a computer simulation. Our results support the possibility that this theory is able to describe accurately the nonergodicity parameters of simple as well as of network-forming liquids.

The quantitative description of the glassy dynamics in liquids is one important goal of modern research in condensed matter. Work in the last decade has provided evidence [1] that the so-called mode-coupling theory (MCT) [2] is able to describe the slow dynamics of *fragile* liquids [3] in the weakly supercooled state. Detailed theoretical predictions for model systems—including hard sphere systems, simple binary liquids, and molecular liquids—have been found to be in remarkable agreement with experimental measurements as well as with simulation results [4–8]. For example, the full q dependence of the Lamb-Mössbauer and of the Debye-Waller factors is predicted well by the theory [2].

Recently, it has been shown that also intermediate and strong glass formers [3], such as glycerol or silica (SiO_2) [9,10], show features that are in *qualitative* agreement with the predictions of MCT. However, in the case of silica, a detailed comparison between theory and numerical data has questioned the ability of MCT to describe correctly the Debye-Waller factors of this important network-forming material [11,12]. In this Letter we show that the disagreement between molecular dynamics (MD) results and theoretical predictions—for the case of silica—was not due to the failure of MCT to describe caging in this network-forming liquid but to a further approximation which is assumed for the sake of simplicity in the commonly used MCT equations. We show that, once this approximation is avoided, MCT is able to describe accurately the cages in silica, opening the way for a full description of dynamics in network-forming liquids above the critical temperature of MCT.

To start we briefly review the MCT equations. The central quantity is the coherent intermediate scattering function $\mathbf{F}(\mathbf{q}, t)$, which for the binary system composed by N particles can be written as a 2×2 matrix with entries $F_{ij}(\mathbf{q}, t) = \langle \delta \rho_i(\mathbf{q}, 0) \delta \rho_j^\star(\mathbf{q}, t) \rangle / N$. Here $\rho_i(\mathbf{q}, t)$ is the density fluctuation for wave vector $\mathbf{q}$, and i is the label for the species. Note that $\mathbf{F}(\mathbf{q}, t = 0)$ is the static structure factor matrix $\mathbf{S}$.

The equation of motion for $\mathbf{F}(\mathbf{q}, t)$ is given by

$$\ddot{\mathbf{F}}(\mathbf{q}, t) + \mathbf{\Omega}^2(q)\mathbf{F}(\mathbf{q}, t) + \int_0^t d\tau \, \mathbf{M}(\mathbf{q}, t - \tau)\dot{\mathbf{F}}(\mathbf{q}, \tau) = 0,$$

(1)

where the frequency matrix is given by $[\mathbf{\Omega}^2(q)]_{ij} = q^2 k_B T (x_i/m_i)[\mathbf{S}^{-1}(q)]_{ij}$. Here $q = |\mathbf{q}|$, x_i is the concentration of species i, and m_i is their mass. Within the framework of MCT, the memory function $\mathbf{M}$ is given by $M_{ij} = x_i k_B T N_{ij}/m_i$, where the matrix N_{ij} is a quadratic form in $F_{ij}(\mathbf{q}, t)$:

$$N_{ij}(\mathbf{q}, t) = \frac{n}{2 x_i x_j} \int \frac{d\mathbf{k}}{(2\pi)^3} \sum_{\alpha\beta} \sum_{\alpha'\beta'} V_{i\alpha\beta}(\mathbf{q}, \mathbf{k})$$
$$\times V_{j\alpha'\beta'}(\mathbf{q}, \mathbf{q} - \mathbf{k}) F_{\alpha\alpha'}(\mathbf{k}, t) F_{\beta\beta'}(\mathbf{q} - \mathbf{k}, t).$$

(2)

Here n is the particle density, and the vertices $V_{i\alpha\beta}(\mathbf{q}, \mathbf{k})$ are given by

$$V_{i\alpha\beta}(\mathbf{q}, \mathbf{k}) = \frac{\mathbf{q} \cdot \mathbf{k}}{q} \delta_{i\beta} c_2^{i\alpha}(\mathbf{k})$$
$$+ \frac{\mathbf{q} \cdot (\mathbf{q} - \mathbf{k})}{q} \delta_{i\alpha} c_2^{i\beta}(\mathbf{q} - \mathbf{k})$$
$$+ nq c_3^{i\alpha\beta}(\mathbf{q}, \mathbf{q} - \mathbf{k}) \cdot x_i.$$

(3)

The function $c_2^{ij}(\mathbf{q}) = n^{-1}(\delta_{ij}/x_i - [\mathbf{S}^{-1}(\mathbf{q})]_{ij})$ is the direct correlation function, and $c_3^{i\alpha\beta}(\mathbf{q}, \mathbf{k})$ is the triple correlation function, which is related to the triple density fluctuations via

$$\langle \delta\rho_\alpha(\mathbf{q})\delta\rho_\beta(\mathbf{k})\delta\rho_\gamma^\star(\mathbf{q} + \mathbf{k}) \rangle = N \sum_{\epsilon\sigma\eta} S_{\alpha\epsilon}(q) S_{\beta\sigma}(k) S_{\gamma\eta}(|\mathbf{q} + \mathbf{k}|)[\delta_{\epsilon\sigma}\delta_{\epsilon\eta}\delta_{\eta\sigma}/x_\epsilon^2 + n^2 c_3^{\epsilon\sigma\eta}(\mathbf{q}, \mathbf{k})].$$

(4)

The only input required by MCT are the *static* quantities $\mathbf{S}$, c_3, and n. Temperature enters the equations only through the explicit T dependence of $\mathbf{\Omega}^2(q)$ and the implicit T dependence of the static quantities. The solution of this type of equation shows at low T a two-step relaxation dynamics, if T is above T_c, the so-called critical temperature of MCT [2].

Below T_c the time correlation functions do not decay to zero anymore, thus signaling that the system is no longer ergodic. Hence the height of the plateau in a time correlation function is usually called the nonergodicity parameter (NEP) since it measures that fraction of the correlation that does not decay to zero even at long times. The Debye-Waller factor $F_c(q)$, the main quantity discussed in this Letter, is defined as the NEP of $F(q, t)$. The physical relevance of the NEP can be inferred from the fact that it can be directly measured in light and neutron scattering experiments.

In one of the first attempts to solve the MCT equations for soft spheres, the possibility of setting in Eq. (3) $c_3 = 0$ was considered [4]. This approximation corresponds to a factorization of the triple density correlation in q space in the products of the three pair density correlation. It was found that for this simple liquid, this approximation does not significantly affect the MCT predictions [4]. Therefore all following MCT studies of simple liquids have assumed $c_3 = 0$. In this Letter we check the validity of this approximation for a network-forming liquid. We use MD simulations to determine the triple correlation function for silica [13] and use these functions to solve the full MCT equations. This calculation allows us to determine for the first time whether or not MCT is able to give a quantitative description of the cages of *strong* glass formers. For the sake of comparison, we perform the same study for a well-studied binary mixture of Lennard-Jones particles (BMLJ) [17].

In the past, the dynamics of both systems has been carefully analyzed and it has been shown that the relaxation dynamics shows the qualitative features predicted by the MCT [10–12,18,19]. For the case of the BMLJ also a quantitative comparison has been made in that $F_c(q)$ has been calculated theoretically (assuming $c_3 = 0$) and compared with simulation data [6]. This comparison showed that very good agreement between theory and simulation is obtained, even if $c_3 = 0$ is assumed, in agreement with the conclusions of Ref. [4]. But for the case of SiO_2 a similar comparison showed that the MCT prediction for $F_c(q)$ does not describe properly the confining cage if $c_3 = 0$ [11,12].

To determine T_c and $F_c(q)$ we have solved the MCT equations [Eqs. (1)–(3)] on a grid of 100 wave vectors with spacing Δ using the iteration procedure from Ref. [4]. For the case of SiO_2 and BMLJ, Δ is 0.154 Å^{-1} and $0.334\sigma_{AA}^{-1}$, respectively. In order to investigate the influence of c_3 it was necessary to determine $c_3^{\epsilon\sigma\eta}(q, k)$ with high precision. Thus we determined all possible triplets of moduli $|k|$, $|p|$, $|q|$, all smaller than 100 Δ, such that $q = k + p$. For each of these triplets of moduli we then picked randomly up to 100 *vectors* k, p, q, and calculated for them the triple density fluctuations $\langle\delta\rho_\alpha(k)\delta\rho_\beta(p)\delta\rho_\gamma^\star(q)\rangle$. Then we used Eq. (4) to determine c_3. For BMLJ we averaged the triple density fluctuations over 12 000 independent configurations (i.e.,

they were separated by more than the typical α-relaxation time), corresponding to a total of 10^8 time steps in the simulation. For SiO_2 we averaged over 2000 independent configurations (2×10^7 time steps).

Note that this very large number of independent configurations was needed in order to determine c_3 with sufficiently high accuracy to make sure that the final results for the NEP do not depend anymore on the noise in c_3. We mention that using only 200 independent configurations was, e.g., not sufficient to guarantee this. Because of the large effort needed to generate the configurations and to analyze them, we determined c_3 only for one temperature, namely, $T = 1.0$ (BMLJ) and $T = 4000$ K (SiO_2). Thus in the calculation of the MCT vertices in Eq. (3) we assumed that the direct correlation functions depend on temperature but that the T dependence of c_3 can be neglected.

The resulting theoretical predictions for the three components of the Debye-Waller factor are shown in Figs. 1 (BMLJ) and 2 (SiO_2). In each panel three curves are shown: the data from the simulations (filled circles) [11,19], the theoretical prediction if $c_3 = 0$ (curves labeled with "c_2"), and the theoretical prediction if c_3 is taken into account (curves labeled with "c_3") [20]. From Fig. 1 we see that the curves for c_2 and c_3 are very
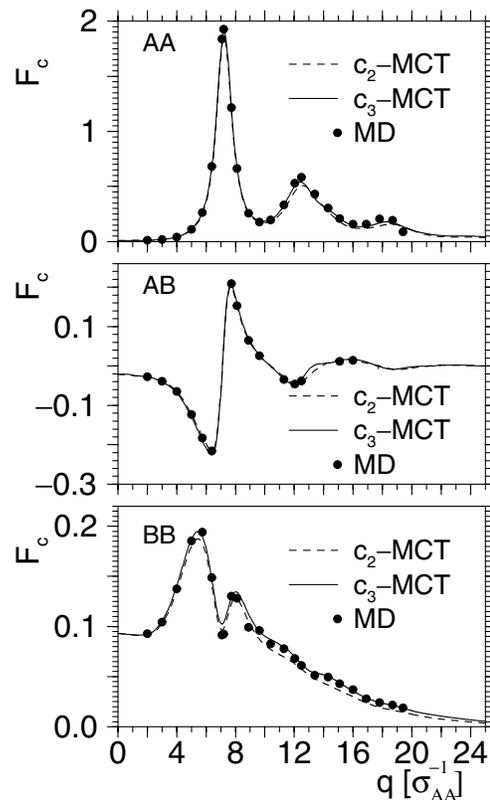

FIG. 1. Wave-vector dependence for the nonergodicity parameters for the BMLJ system. The solid and dashed curves are the theoretical predictions with and without the inclusion of the c_3 terms in Eq. (2). The circles are the MD results from [19].
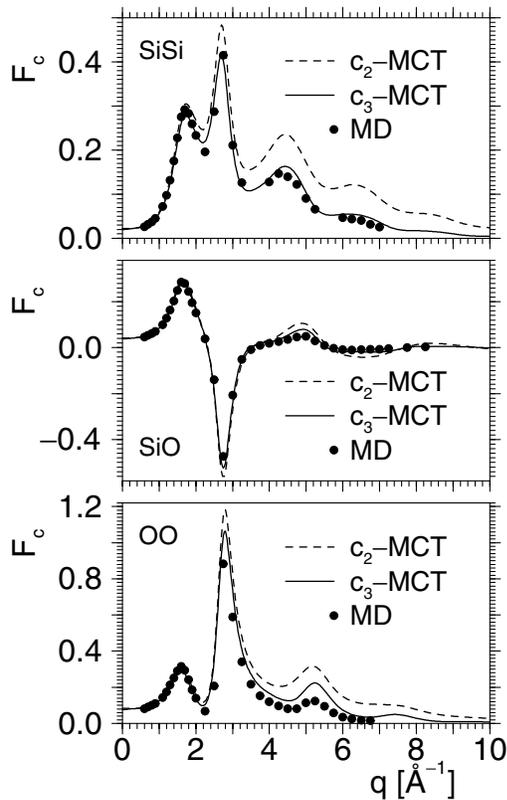
FIG. 2. The same quantities as in Fig. 1, but for silica. The MD data are from Ref. [11].

close together, from which we conclude that in the case of the BMLJ the inclusion of c_3 changes the prediction of the theory only weakly. The main difference between the two curves is in the *BB* correlation, where the c_3 curve describes the simulation data better than the c_2 curve. Also the theoretical prediction for T_c is essentially independent of whether or not c_3 is neglected, in that T_c decreases from $T_c = 0.922$ to $T_c = 0.910$ if c_3 is taken into account. These results are in agreement with the findings of Ref. [4].

From Fig. 2 we recognize that for the case of SiO_2 the influence of c_3 on the NEP is much stronger than for the BMLJ system. For this network-forming liquid the inclusion of c_3 into the vertices leads to predicted curves $\mathbf{F}_c(q)$ which are in substantially better agreement with the ones from the simulation than the ones from the c_2 theory. The improvement is particularly noticeable for q above the location of the first peak, a length scale that corresponds to the distance between two neighboring tetrahedra. For example, in the case of the Si-Si correlation the relative difference between the theoretical curve and the MD data is decreased by a factor around 5. The remaining difference is now only on the order of the error of the MD data.

Note that $\mathbf{F}_c(q)$ provides partial information on the cage in which a particle is confined and which is formed by its neighboring particles [21]. The fact that in the vicinity of the first maximum the two theoretical curves as well as the

MD data are very close together shows that already the c_2 theory is able to capture the structure of the cage on this length scale. For larger wave vectors the c_2 curve is too high, which means that the size of the cage is underestimated. Only if the terms due to c_3 are taken into account, can a reliable description for the cage be obtained.

For the Si-Si correlation the mentioned decrease of the NEP is more pronounced than for the two other correlation functions, which is reasonable since it is the Si atoms that sit in the center of the tetrahedra, i.e., that make up the network structure, and hence it can be expected that the inclusion of the c_3 terms is important. Nevertheless, from the figure we see that the inclusion of these terms leads also to a significant improvement of the theoretical prediction for the NEPs for Si-O and O-O if q is larger than the location of the first peak. Thus we conclude that the c_2 MCT is able to give a good description of the cage for the oxygens only on the length scale corresponding to the first maximum of $\mathbf{F}(\mathbf{q}, 0)$.

The strong influence of the c_3 terms on $\mathbf{F}_c(q)$ is also found in the value of T_c. If one sets $c_3 = 0$, one finds $T_c = 3962$ K, whereas the c_3 theory predicts $T_c = 4676$ K. Thus, whereas for the BMLJ system we found only a change of the order of 1%, we now find a change around
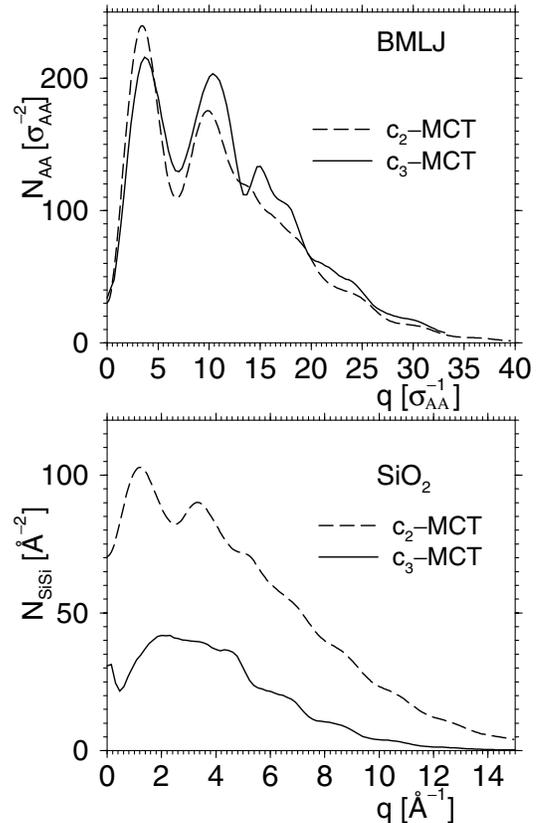

FIG. 3. Wave-vector dependence of $N_{AA}(q, \infty)$ and $N_{SiSi}(q, \infty)$ (upper and lower panels, respectively). The labeling of the curves is as in Fig. 1.

18%. We mention, however, that MCT usually overestimates the value of T_c, and indeed we have $T_c^{\mathrm{MD}} = 0.435$ and $T_c^{\mathrm{MD}} = 3330$ K for BMLJ and SiO$_2$, respectively [10,18].

Finally we show in Fig. 3 the q dependence of $N_{AA}(q, \infty)$ and $N_{\mathrm{SiSi}}(q, \infty)$ from Eq. (2) at the corresponding T_c. From this figure we see that for the BMLJ case the c_2-memory function is very similar to the one in which c_3 is taken into account and thus it is not surprising that also the NEP and the T_c are not changing. This is in stark contrast to the SiO$_2$ system, for which the memory functions from the c_2 and c_3 theories are very different. Note that in a binary mixture each component of the memory function has contributions from 16 different terms [see Eq. (2)]. We found that in the case of SiO$_2$ the inclusion of the c_3 terms leads to a significant change of the contribution involving the off-diagonal terms. In the c_2 case these contributions are *negative,* thus they drive the transition to lower temperatures. If the c_3 terms are taken into account, these contributions become less negative and hence the transition takes place already at higher temperatures.

In summary, the present calculation shows that MCT is able to give an accurate *quantitative* description of the NEP for a strong glass former. This opens the way for a detailed description of the dynamics in the MCT region for this class of materials. Hence our results support the possibility that MCT is able to make quantitative predictions for all types of glass formers.

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[13] The potential used to describe silica is the one proposed by van Beest *et al.* [14] and which has the functional form $V_{\alpha\beta}(r) = q_\alpha q_\beta / r + A_{\alpha\beta} q_\beta \exp(B_{\alpha\beta} q_\beta r) - C_{\alpha\beta} q_\beta / r^6$, with $\alpha, \beta \in \{\mathrm{Si}, \mathrm{O}\}$. The values of the parameters q_α, $A_{\alpha\beta}$, $B_{\alpha\beta}$, and $C_{\alpha\beta}$ can be found in Ref. [14]. Despite its simplicity, this potential has been shown to give a reliable description of the static and dynamical quantities of real SiO$_2$ [10,15,16]. In particular, it is able to reproduce its open network structure. In the present simulation we used 600 ions in a box of $(20.4 \text{ Å})^3$.

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[21] In a glass, the size of the cage can be determined measuring the width in q space of the *incoherent* (self) intermediate scattering function NEP [2]. At large q, the *coherent* NEP approximates well the *incoherent* NEP. In this regard, partial information on the cage size can be obtained from the study of $\mathbf{F_c}(q)$.