

Critical test of the mode-coupling theory of the glass transition

Ludovic Berthier¹ and Gilles Tarjus²

¹*Laboratoire des Colloïdes, Verres et Nanomatériaux, Université Montpellier II and UMR 5587 CNRS, 34095 Montpellier, France*

²*LPTMC, CNRS-UMR 7600, Université Pierre et Marie Curie, Boîte 121, 4 Place Jussieu, 75252 Paris Cedex 05, France*

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In its common implementation, the mode-coupling theory of the glass transition predicts the time evolution of the intermediate scattering functions in viscous liquids on the sole basis of the structural information encoded in two-point density correlations. We provide a critical test of this property and show that the theory fails to describe the strong differences of dynamical behavior seen in two model liquids characterized by very similar pair-correlation functions. Because we use “exact” static information provided by numerical simulations, our results are a direct indication that some important information about the dynamics of viscous liquids is not captured by pair correlations and is thus not described by the mode-coupling theory, even in the temperature regime where the theory is usually applied.

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I. INTRODUCTION

Near the glass transition, the viscosity of a supercooled liquid is very sensitive to small temperature changes, and structural relaxation is likely a thermally activated process over an effective free-energy barrier E , which grows upon cooling, $\eta(T) \sim \eta_\infty \exp[E(T)/k_B T]$. From a theoretical perspective, one wishes to understand and provide accurate predictions for $E(T)$ in terms of the microscopic interactions between particles in the liquid. However, even for the simple case of spherical particles with short-ranged pairwise interactions, establishing a link between microscopic interactions and structural relaxation remains an open theoretical challenge [1].

In this paper, we assess one of the theoretical approaches of the glass transition, the mode-coupling theory (MCT). The theory emerged in the mid-1980s in the context of the theory of simple liquids and provided predictions for the time evolution of density autocorrelation functions from the knowledge of the interaction between the particles [2]. These detailed predictions come at the expense of a number of approximations. First, density fluctuations are selected as the relevant slow variables. Then, all forces are projected onto density fluctuations as well. This is the step of interest for us here, because it follows that microscopic interactions enter the dynamical equations of motion in the form of pair and triplet correlations, with the latter having little influence for the Lennard-Jones (LJ) interactions studied in the present work [3] and being routinely neglected. Finally, a Gaussian factorization of four-point dynamic correlators is performed to close the dynamical equations onto two-body correlators. It is presumably this final step which is responsible for the appearance of a power-law singularity of the relaxation time and the well-known failure of MCT to describe “activated processes” in deeply supercooled liquids [4–6].

It is obvious that the evolution of the pair-correlation function must have at least some influence on the dynamics. Accordingly, some of the predictions that are obtained within MCT compare reasonably well to numerical or experimental work. For instance, MCT provides guiding information in those cases where the changes in the static pair-correlation

functions brought about by adding every short-range attractions [7], asphericity [8], or particle softness [9] to a dense system of hard spheres appear mostly responsible for the changes in dynamics reported for these systems.

There are however also indications in the literature that there may be relevant structural information which is not captured by two-point functions. For instance, extreme cases have been devised in which the slowdown of relaxation takes place in the complete absence of pair correlations among particles [10–12]. Broadly speaking, it is often stated that some form of “local order” grows upon decreasing the temperature in supercooled liquids [1]. This order can be, for instance, (frustrated) icosahedral order [13] or the less well characterized “amorphous order” encoded in high-order “point-to-set” correlation functions [14]. In both cases, $g(r)$ is essentially blind to this growing static order, and the effect of the latter on the dynamics (if any) would be completely missed by MCT. Similarly, it is by now understood that structural relaxation near the glass transition occurs in a spatially correlated manner, with a dynamic length scale that grows upon cooling, with again no corresponding change in the pair-correlation function [15].

Recently, we found that two model liquids with very similar structure at the level of pair-correlation functions display distinct behavior upon cooling [16]. More specifically, we studied a binary LJ mixture [17] and the corresponding repulsive “Weeks-Chandler-Andersen (WCA) mixture” in which attractive forces are truncated beyond the minimum of the pair potential [18], and we showed that the presence or absence of the attractive forces determines to a great extent the apparent energy barrier to structural relaxation and its evolution with temperature and density. Therefore, these two model systems represent a benchmark on which the above ideas can be tested in much detail.

In a previous work, Voigtmann used liquid-state theory to obtain the pair-correlation function of the Lennard-Jones and the associated repulsive WCA models in the monatomic case [19]. He then introduced the results in the MCT equations and found that the two liquids were essentially sharing the same dynamics, with nearly identical MCT critical temperatures. In our simulations, on the other hand, we use a binary mixture, and we detect small differences between the struc-

tures of the two models. Thus, we directly insert the exact (numerically determined) structure factors into the MCT equations to test with a greater sensitivity the response predicted by MCT to small structural changes. Our main conclusion is that MCT fails to describe the difference in the dynamical behavior of the two liquids. More generally, this conclusion also suggests that microscopic theories of the glass transition based on pair-correlation functions cannot accurately predict the evolution of the structural relaxation time.

In Sec. II we describe our models and method of analysis. In Sec. III we present our results for the dynamics. Section IV concludes the paper.

II. MODELS, METHODS, AND STATIC RESULTS

A. Static structure

We consider the binary mixture of Lennard-Jones particles introduced by Kob and Andersen [17], as well as its WCA truncation [18]. The system is a 80:20 mixture of $A:B$ particles interacting with the following interatomic pair potential between species α and β , with $\alpha, \beta = A, B$:

$$v_{\alpha\beta}(r) = 4\epsilon_{\alpha\beta} \left[\left(\frac{\sigma_{\alpha\beta}}{r} \right)^{12} - \left(\frac{\sigma_{\alpha\beta}}{r} \right)^6 + C_{\alpha\beta} \right], \quad r \leq r_{\alpha\beta}^c, \quad (1)$$

and $v_{\alpha\beta}(r > r_{\alpha\beta}^c) = 0$. In this expression, the cutoff distance $r_{\alpha\beta}^c$ is equal to the position of the minimum of $v_{\alpha\beta}(r)$ for the WCA potential and to a conventional cutoff of $2.5\sigma_{\alpha\beta}$ for the standard LJ model; $C_{\alpha\beta}$ is a constant such that $v_{\alpha\beta}(r_{\alpha\beta}^c) = 0$. The value of the parameters $\sigma_{\alpha\beta}$ and $\epsilon_{\alpha\beta}$ were designed to obtain good glass-forming ability [17].

We perform molecular-dynamics simulations of both systems in the NVE ensemble after proper equilibration at a chosen state point characterized by a density ρ and a temperature T . We use $N=900-1300$ particles (depending on the density) and work with periodic boundary conditions. A broad range of densities has been considered with ρ varying from 1.2 to 1.6. Lengths, temperatures, and times are given in units of σ_{AA} , ϵ_{AA}/k_B , and $(m\sigma_{AA}^2/48\epsilon_{AA})^{1/2}$, respectively. In line with the WCA theory [18], the two liquid models are compared at the same (ρ, T) state points. Their pressures then differ, with the attractive interaction roughly providing a temperature-independent negative shift. This also explains why we perform comparisons at constant density instead of the constant pressure conditions that would be more naturally expected from experimental considerations.

From the numerical simulations we obtain both static and dynamic properties. We use static information as input for the MCT analysis described below, while the dynamical data are used to test the accuracy of the theoretical results. For the dynamics, we record the evolution of the time dependence of the self-part of the intermediate scattering function,

$$F_s^\alpha(q, t) = \frac{1}{N_\alpha} \left\langle \sum_{j=1}^{N_\alpha} e^{i\mathbf{q} \cdot [\mathbf{r}_j^\alpha(t) - \mathbf{r}_j^\alpha(0)]} \right\rangle, \quad (2)$$

with $q\sigma_{AA} \approx 7.2$, which corresponds to the position of the peak of the total static structure factor at $\rho=1.2$ (see Fig. 1).

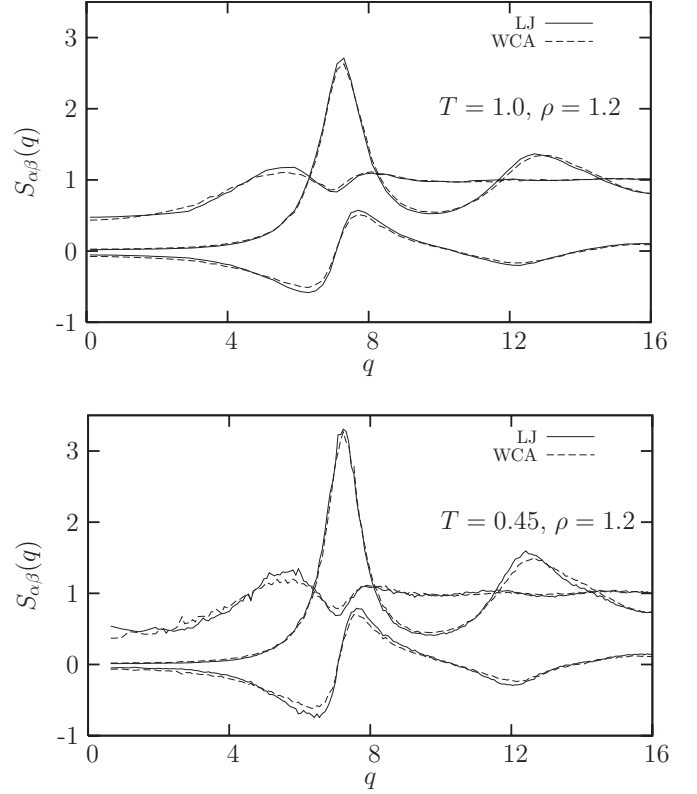


FIG. 1. Partial static structure factors $S_{BB}(q)$, $S_{AA}(q)$, and $S_{AB}(q)$ (from top to bottom at small q) at $\rho=1.2$ near the theoretically determined T_c of MCT (top) and close to the T_c obtained from fitting the simulation data (bottom). The pair structures of the LJ and WCA liquids are very close, and the small deviations seem to increase somewhat when T decreases.

In this expression, N_α denotes the number of particles of species α , and $\mathbf{r}_j^\alpha(t)$ is the position of particle j belonging to species α at time t . From the decay of $F_s^\alpha(q, t)$ for the majority species $\alpha=A$, we obtain the relaxation time $\tau(\rho, T)$, which we conventionally define as $F_s^A(q, \tau) = 1/e$. Some of the data for $\tau(\rho, T)$ were presented in Ref. [16].

At the structural level, we measure the partial structure factors $S_{\alpha\beta}(q)$ which are needed as input for the MCT calculations. They are defined as

$$S_{\alpha\beta}(q) = \frac{1}{\sqrt{N_\alpha N_\beta}} \sum_{m=1}^{N_\alpha} \sum_{n=1}^{N_\beta} e^{i\mathbf{q} \cdot (\mathbf{r}_m^\alpha - \mathbf{r}_n^\beta)}, \quad (3)$$

which can be written in a more compact form as a 2×2 matrix $\mathbf{S}(q)$ whose matrix elements are the partial structure factors $S_{\alpha\beta}(q)$.

We present a set of representative results for the partial structure factors in Fig. 1 for $\rho=1.2$ and in Fig. 2 for $\rho=1.6$. The former corresponds to the canonical density at which the Kob-Andersen mixture is usually studied [17]. For each density, we present the data at two temperatures, corresponding to the location of the MCT transition determined either theoretically or by fitting the simulation data. Generically, the latter is lower than the former.

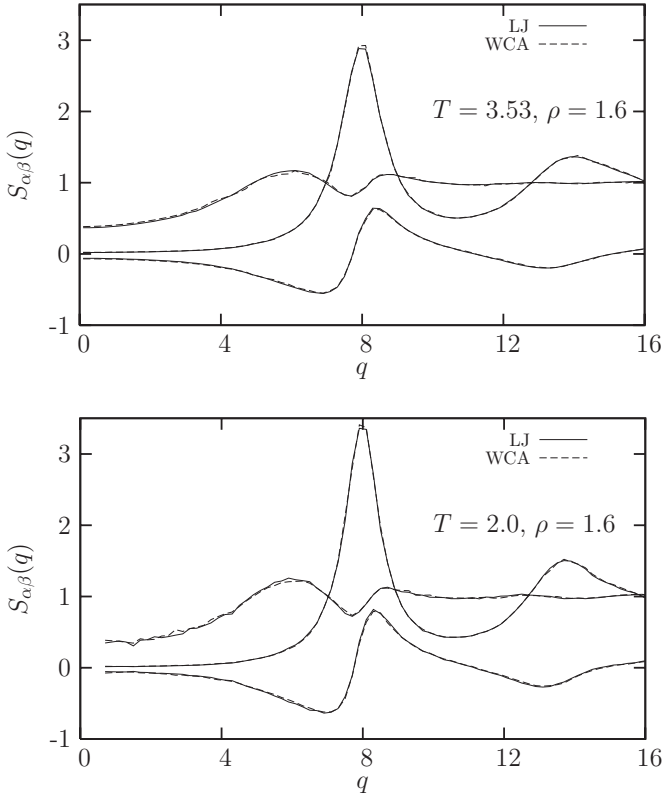


FIG. 2. Same as Fig. 1 for $\rho=1.6$. Here, the agreement between LJ and WCA mixtures is nearly perfect at all temperatures.

These data confirm the well-known fact that the LJ and WCA models have a pair structure which is very similar, even in the case of a binary mixture. This supports the idea that the contribution of the attractive forces at the level of the two-point structure can be considered as a small perturbation and treated as such in theoretical liquid-state calculations [18]. Looking more closely, we can nevertheless detect some small differences between the two systems. These differences increase slightly when one lowers the temperatures at constant density, as can be concluded, for instance, by comparing the two panels in Fig. 1. The agreement between the pair structures of the two liquids becomes excellent when density increases (see Fig. 2). This is physically reasonable since the steep repulsive core of the pair potential in Eq. (1), which is the same for both models, should play a more dominant role at larger densities.

We have obtained $\mathbf{S}(q)$ for a large number of state points at the densities $\rho=1.2, 1.4$, and 1.6 . We have then proceeded in two steps. First, we have directly inserted those data into the MCT dynamical equations presented below to obtain a rough determination of the location of the MCT transition. Then, we have used a smooth interpolation procedure to obtain the partial structure factors in a small temperature window near the transition, because it is not possible to resolve the structure directly from simulations with the accuracy needed to characterize the MCT transition. This interpolation procedure is however quite innocuous, as the structure evolves in a mild and continuous manner in the temperature regime where the interpolation has to be performed.

B. Mode-coupling theory

The mode-coupling theory of the glass transition [2] was originally derived to describe the dynamics of Newtonian systems [20]. A somewhat different derivation was also provided in the framework of the nonlinear fluctuating hydrodynamics [21]. An analogous theory was later derived for Brownian systems [22]. Here, we briefly present the latter version of MCT which, for convenience, we use in the following.

The starting point of the theory is an exact equation for the time evolution of the intermediate scattering functions $\mathbf{F}(q, t)$ in terms of the so-called irreducible memory function,

$$\frac{\partial}{\partial t} \mathbf{F}(q, t) = -D_0 q^2 \mathbf{S}^{-1}(q) \mathbf{F}(q, t) - \int_0^t dt' \mathbf{M}(q, t-t') \frac{\partial}{\partial t'} \mathbf{F}(q, t'). \quad (4)$$

In this equation, D_0 is the diffusion coefficient of an isolated Brownian particle, and $\mathbf{F}(q, t)$ is a matrix whose elements are the intermediate scattering functions $F^{\alpha\beta}(q, t)$ defined as

$$F^{\alpha\beta}(q, t) = \frac{1}{\sqrt{N_\alpha N_\beta}} \sum_{m=1}^{N_\alpha} \sum_{n=1}^{N_\beta} e^{i\mathbf{q} \cdot [\mathbf{r}_m^\alpha(t) - \mathbf{r}_n^\beta(0)]}, \quad (5)$$

and is such that $\mathbf{F}(q, t=0) = \mathbf{S}(q)$. The matrix of memory functions, $\mathbf{M}(q, t)$, can be expressed, in the mode-coupling approximation, in terms of the intermediate scattering functions \mathbf{F} and structure factors \mathbf{S} . The corresponding (lengthy) expression can be found in Ref. [24].

Equation (4) allows us to evaluate the time dependence of the intermediate scattering functions. The only input required is the static structure factor $\mathbf{S}(q)$. It is easy to see that the natural time unit for our system is σ^2/D_0 . In the following, all times are given in terms of this unit.

The numerical resolution of Eq. (4) is difficult because one needs to describe the evolution of the intermediate scattering function on very widely separated time scales. The commonly used algorithm was first described in Ref. [23]; here, we use the implementation described in great detail in Ref. [24]. Briefly, the basic steps of the algorithm are as follows. The integro-differential equation is discretized and solved numerically for $2N_s$ steps with a finite time step of δt . After $2N_s$ steps are completed, the time step is doubled, and the results from the initial $2N_s$ steps are mapped onto a new equally spaced set of N_s values for the quantities needed to continue the numerical algorithm. This mapping includes the integrals as well as the intermediate scattering functions. Then, the numerical algorithm is restarted with the new time step and proceeds for another N_s time steps, and the mapping is performed again. This procedure is followed until a convergence condition is satisfied. In the present work we used 200 equally spaced wave vectors with spacing $\delta=0.2$, with the first wave vector being at $k_{\min} = \delta/2$ and the largest wave vector being at $k_{\max} = 39.9$.

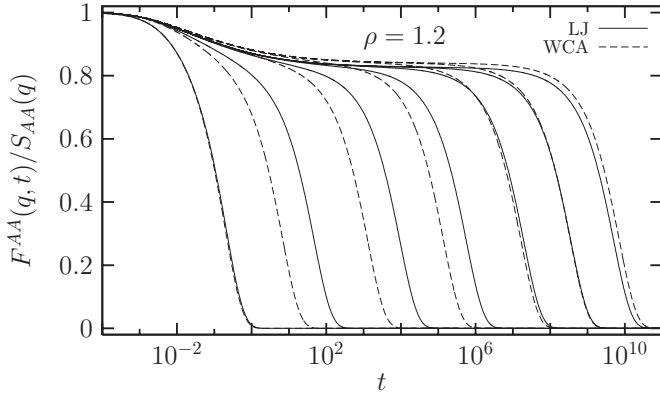


FIG. 3. Normalized intermediate scattering function for the majority component for $\rho=1.2$ and $q=7.1$, for both LJ (full lines) and WCA (dashed lines) models obtained from the numerical solution of Eq. (4). The temperature decreases from left to right. LJ: $T = 3.0, 1.0, 0.908, 0.899, 0.8975, 0.8972, 0.8971$. WCA: $T = 3.0, 1.0, 0.77, 0.746, 0.7425, 0.7421, 0.74198$. Note that the two sets of temperatures are not identical. The lower temperatures in each set provide a good estimate of the T_c values for each model.

III. DYNAMICAL BEHAVIOR

A. Intermediate scattering functions

The solution of the MCT dynamical equations provides the time evolution of the intermediate scattering functions $F^{\alpha\beta}(q, t)$. We present a selection of data for the majority component, $\alpha=\beta=A$, at density $\rho=1.2$ in Fig. 3. These data have the standard shape obtained within MCT, whereby the time decay stretches over many decades of time when approaching the MCT singularity and occurs in two widely separated time scales. From now on, we focus on the slower of these, corresponding to the structural (alpha) relaxation of the system. Its time dependence is empirically well described by a stretched exponential form,

$$F(q, t) \sim \exp[-(t/\tau)^\beta], \quad (6)$$

as commonly found in supercooled liquids. The data in Fig. 3 suggest that the stretching exponent β is essentially the same at all temperatures (and so MCT data obey a time-temperature superposition property) and is very close for both LJ and WCA liquids, with $\beta \approx 0.87$. We find similar values and agreement for all densities up to $\rho=1.6$. For $\rho=1.2$ and $q=7.25$, Kob and Andersen reported a similar value, $\beta=0.85$ [25].

The intermediate scattering functions of the two models superimpose at very high temperatures, $T=3.0$, when the structure factors also show very good agreement. However, when temperature is decreased, the dynamics of the WCA model becomes faster than that of the LJ model; see the data for $T=1.0$ in Fig. 3. The difference becomes more dramatic as the mode-coupling singularity is approached and long relaxation times are obtained. Although this is reminiscent of our numerical findings on the role of attractive forces in supercooled liquids [16], we shall see below that MCT only marginally accounts for this effect.

As in numerical simulations, we determine the structural relaxation time $\tau(T, \rho)$ through the relaxation $F^{\alpha\beta}(q, \tau)/S_{\alpha\beta}(q)=1/e$. This relaxation time depends on the wave vector q , the chosen species α and β . It is *a priori* different from the time extracted from simulations where only the incoherent part of the intermediate scattering function is considered. However, a simplifying feature of MCT calculations is that the evolution of τ is the same for all observables near the transition. Thus, it does make sense to focus on a given wave vector (provided it roughly corresponds to typical interatomic distances: here, we choose the maximum of the first diffraction peak), to focus on the majority component of the liquid ($\alpha=\beta=A$), and to compare these results to the simulation data for which the incoherent scattering function is measured.

The only difference between the two sets of data shown in Fig. 3 lies in the temperature regimes they cover since the MCT transition of the WCA model occurs at a slightly lower temperature than that of the full LJ model including the attractive component of the potential. We now turn to a more precise discussion of this difference.

B. Relaxation times

We now enter the core of our analysis and study in detail the evolution with T and ρ of the structural relaxation time, as predicted by MCT, and compare these theoretical results to those from computer simulations. We first present in Fig. 4 our results in an Arrhenius plot, showing the evolution of $\tau(T, \rho)$ on a logarithmic scale against the inverse temperature $1/T$, for both the LJ and the WCA models, as measured in MCT calculations and in simulations. We show results for $\rho=1.2$ and $\rho=1.6$.

In this Arrhenius representation, the results of MCT calculations appear almost “vertical,” because MCT predicts the existence of a critical singularity T_c at which the relaxation time diverges algebraically [2]. This divergence is not seen in computer simulations, and so the simulation data look qualitatively different.

A second striking observation from Fig. 4 is that MCT clearly overestimates the temperature regime where slow dynamics sets in by about 100%. Thus, there is no range of temperature where the theoretical calculations follow the simulation results, even if a vertical shift (corresponding to a trivial rescaling of the microscopic time scale) is allowed.

At high temperatures, a good empirical representation of both MCT and simulation results is obtained by introducing an Arrhenius-like temperature dependence,

$$\tau \sim \tau_\infty \exp\left(\frac{E_\infty}{T}\right). \quad (7)$$

Although there is no specific theoretical foundation for such a fit, it often accounts quite well for high-temperature results, even in experiments [26]. When fitting the data to Eq. (7), we obtain the values $E_\infty \approx 5.5$ and $E_\infty \approx 4.2$ for the LJ and WCA systems within MCT, while the corresponding simulation data are characterized by $E_\infty \approx 2.55$ and $E_\infty \approx 2.0$. The different values found for the two models in the high-temperature regime reflect the fact that attractive forces already play an

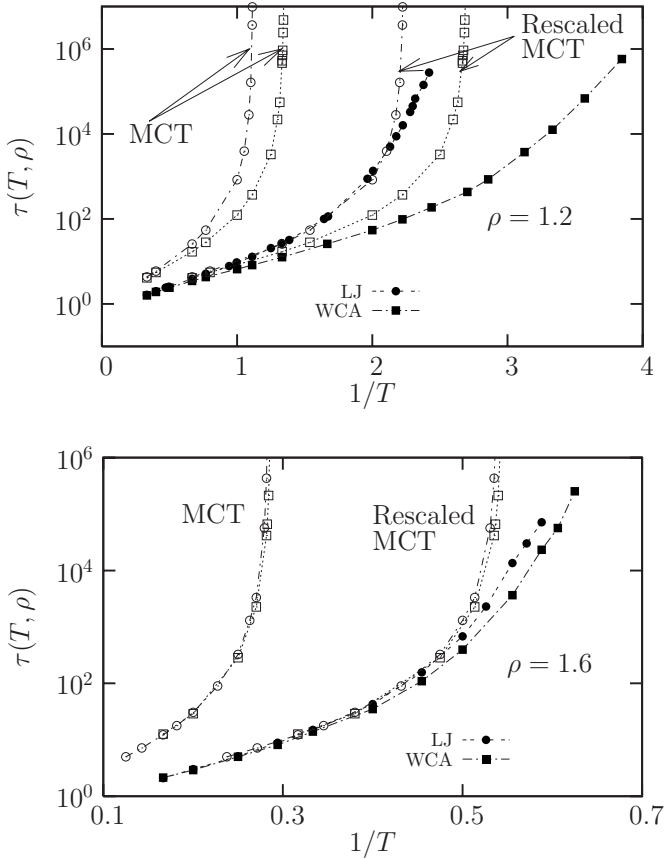


FIG. 4. Comparison of the relaxation times obtained by MCT (open symbols) and simulations (filled symbols) at $\rho=1.2$ (upper panel) and $\rho=1.6$ (lower panel). We both show the bare MCT data and the data rescaled to provide the best collapse of the LJ data. The rescaling factors for the temperature are 2 for $\rho=1.2$ and 1.9 for $\rho=1.6$. These same factors are then applied with no further changes to the WCA model and the obtained curve does not describe the WCA data well.

important quantitative role in this regime, despite the very little changes observed in static quantities. This effect was reported before in the case of simple liquids [27–29].

The role of attractive forces at high temperatures is partially captured by our MCT calculations since we find theoretically a 25% change in E_∞ between the two models. However, given that the predicted values are off by a factor of 2, this agreement could well be fortuitous. At a density $\rho=1.6$, we find $E_\infty \approx 12$ from simulations of the two systems, while MCT again overestimates this value and predicts $E_\infty \approx 22.5$ for both models. So, at high temperatures and large densities, the difference between LJ and WCA mixtures vanishes both in simulations and MCT calculations, but the activation energy predicted by the latter is still in error by a factor close to 2. It is interesting to note that there is nearly the same factor of 2 in error for E_∞ and for T_c (see below), which suggests that MCT does not merely “break down” at low T but is in fact always quite inaccurate in its quantitative predictions for the temperature evolution of the structural relaxation time, even in the high-temperature liquid [30].

The strong disagreement between MCT results and simulations is well known [2] and is twofold: (i) MCT overesti-

mates the temperature regime where slow dynamics takes place and (ii) the predicted algebraic divergence of the relaxation time is not observed. When fitting data to MCT predictions, one can thus only find a modest temperature regime where an algebraic divergence describes the data, and one must simultaneously resort to some sort of rescaling or shift of the control parameters. Since this gives considerable freedom in the data treatment, we adopt the following procedure, shown in Fig. 4. At a given density, we first concentrate on the LJ model. We then rescale τ and T by adjustable time and temperature scales in order to obtain the “best” collapse of theory and simulations. We obtain temperature scaling factors of 2 for $\rho=1.2$ and 1.9 for $\rho=1.6$, which mirror the factor of 2 in E_∞ found above at high temperatures. Once this rescaling is performed for the LJ model, we use the same scaling factor for temperature in the WCA model. The results are presented in Fig. 4. While the rescaling works well if T is not too low in the LJ system, it performs very poorly for WCA, even when density is as large as $\rho=1.6$. This implies that the different dynamical behaviors observed in simulations for LJ and WCA models [16] are only qualitatively reproduced by MCT and are considerably underestimated by the theory at a quantitative level.

This last statement can be made more precise by determining the location of the MCT singularity. We first determine T_c within the theory by following the growth of τ near the transition, which is well described by an algebraic divergence:

$$\tau \sim (T - T_c)^{-\gamma}. \quad (8)$$

The value of the critical exponent γ depends in principle on the studied model. In Fig. 5, we show however that the value $\gamma=2.4$ actually describes both the LJ and the WCA models for densities $\rho=1.2, 1.4$, and 1.6 . The values of the critical temperatures are reported in Table I: T_c increases by a factor of ≈ 4 when density increases from 1.2 to 1.6. As density increases, the difference in critical temperatures between the LJ and WCA models becomes smaller, decreasing from 17% at $\rho=1.2$ to 1% at $\rho=1.6$ within the theory.

While the determination of T_c is unambiguous in MCT calculations, this is not the case in simulations where the MCT power law cannot be followed for arbitrarily large relaxation times. In practice, this means that the fitted values of T_c and γ obtained from simulation data are strongly correlated and therefore depend on the chosen temperature range for fitting. Thus, we decided to constrain our data analysis by imposing the value of the exponent γ obtained in the theoretical calculations. We then determined the value of T_c that fits the data best with the exponent $\gamma=2.4$. The quality of the fits can be judged in Fig. 5, where the data for $\tau(T, \rho)$ are plotted as a function of the reduced variable $(T - T_c)/T_c$ in a log-log representation where Eq. (8) should appear as a straight line. The fit holds over about 2–3 decades in relaxation time, as commonly found in the analysis of numerical and experimental data [2], and deviations at low temperatures occur similarly for both models at all densities. As noted before [24], it should be remarked that the algebraic fit to simulation data is obtained in a range of $(T - T_c)/T_c$ where

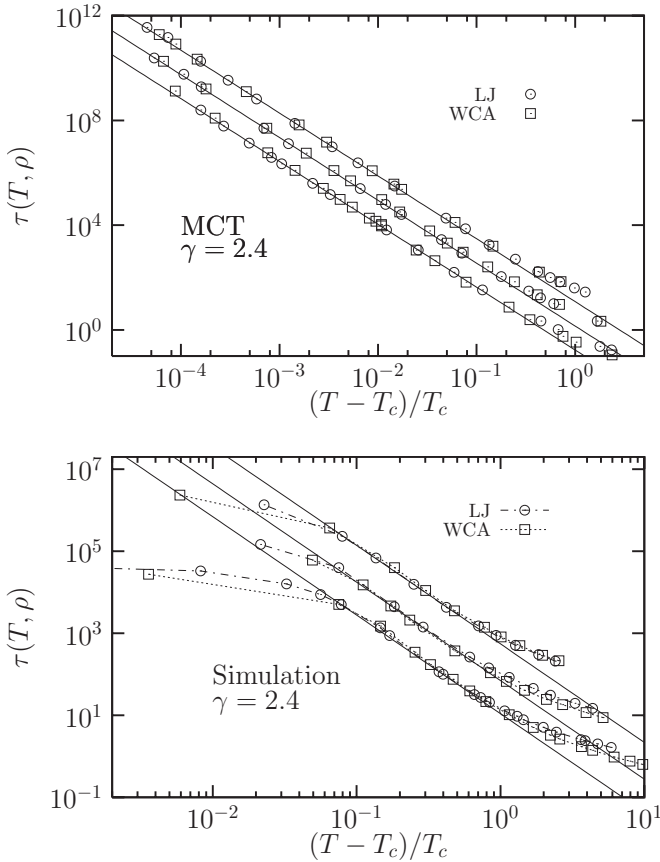


FIG. 5. MCT plot of the relaxation times for $T > T_c$ in which the algebraic divergence in Eq. (8) appears as a straight line. Top: theoretical curves fitted with the same $\gamma=2.4$ for $\rho=1.2, 1.4,$ and 1.6 (from bottom to top). Bottom: same for numerical simulations, but note the difference in scales and the deviations occurring at low temperatures. Data at different densities are vertically shifted, for clarity. Shift factors are 1, 10, and 100 for LJ, and 0.4, 6, and 100 for WCA. Note that contrary to Fig. 4 the simulation data for LJ and WCA are now scaled to different values of T_c .

the theoretical predictions have not yet entered the critical regime, which casts some doubts on the consistency of the fitting procedure.

The values of the critical temperatures obtained by fitting the simulation data are also reported in Table I. The values for the LJ model are very close to those used in Fig. 4 for rescaling the simulation data. (The rescaled MCT plots in Fig. 4 and the fits shown in the lower panel of Fig. 5 are thus fully compatible for the LJ model; on the other hand, we

TABLE I. Theoretical critical temperatures T_c for the LJ and WCA models at different densities, and comparison with estimates from fits to the simulation data.

	1.2	1.4	1.6
LJ-MCT	0.8971	1.8677	3.528
LJ simulation	0.435	0.93	1.76
WCA-MCT	0.7419	1.7707	3.489
WCA simulation	0.28	0.81	1.69

have in purpose not used T_c of the WCA model in Fig. 4 in order to illustrate the ability of MCT to capture the difference of dynamical behavior between LJ and WCA models.) As found theoretically, the difference between the LJ and WCA models is smaller at larger density, when the structure factors become more similar (see Fig. 2). However, the difference in critical temperatures decreases from 36% at $\rho = 1.2$ to 4% at $\rho=1.6$ and is much larger than the MCT theoretical predictions at all densities (respectively, 17% and 1%). Thus, the difference in the dynamical behavior of the two models is only marginally captured by MCT calculations and is quantitatively considerably underestimated.

IV. DISCUSSION

The structure of simple liquids is usually described in terms of pair-correlation functions, and the development of analytical theories to predict their evolution with density or temperature from the knowledge of the interaction between particles has been a major theoretical achievement [31]. Whether knowledge of $g(r)$ is enough to characterize the structure and predict the dynamics of viscous liquids has however been an open question in the field of the glass transition. This is a central issue for mode-coupling theory which, in its common implementation, makes dynamical predictions from the sole knowledge of two-point density correlations.

To address this issue we have used the pair-correlation functions taken from molecular-dynamics simulations to obtain MCT predictions for the relaxation time of two model liquids characterized by similar pair structures, but very distinct dynamics [16]. We have found that MCT is unable to account for these dynamical changes in any quantitative way. In this case at least, the necessary structural input for the dynamics of the viscous liquids is not merely encoded in two-point density correlation functions. Accordingly, MCT is bound to yield quantitatively inaccurate predictions. We note that some small predicted changes are qualitatively correct, such as the relative evolution of the high-temperature effective activation energy E_∞ or the location of the mode-coupling transition T_c , but they superimpose on MCT predictions that are wrong by a factor of 2 in absolute values. As mentioned in the introduction, there still remains a room for applying MCT, as there exists physically relevant glassy phenomena associated with important changes in the structure that are captured by two-body correlations.

In a similar vein, the present work has been an opportunity to test the idea, popularized in particular in the context of MCT, that even small changes in the pair structure may have dramatic consequences in the dynamics. For the case under study, we have found that the small differences seen between the structure factors of the two liquid models only produce, within MCT, minor dynamical differences, thus confirming Voigtmann's results [19]. As already stated, these MCT predictions dramatically underestimate the dynamical changes observed in the simulations. An additional factor explaining this discrepancy is the fact that MCT overestimates by a large amount the location of the putative singularity (empirically estimated by fitting simulation data). As a

result, MCT predictions are based on structure factors measured at relatively high temperatures where differences between the WCA and LJ models are even less pronounced (compare both panels in Fig. 1).

Finally, as mentioned in the introduction, our work does not address whether the failure of “ $g(r)$ determines the dynamics” MCT motto that is shown here is connected to the failure of MCT to describe activated dynamics at low temperatures. For instance, in their attempt to incorporate activated processes in the MCT framework, Schweizer and co-workers [32] managed to avoid the MCT algebraic divergence of Eq. (8). However, in their approach, it is still the pair-correlation function which determines the amplitude of the free-energy barriers that have to be crossed dynamically. It would thus be interesting to check whether in this formulation too, a $g(r)$ -based theory misses the difference of dynamical behavior between the LJ and WCA liquid models, despite the presence of activated processes.

To conclude, our present and previous [16] works show that structural information not incorporated in two-body

density correlations likely plays an important part in driving the slowdown of dynamics in viscous liquids. This raises serious doubts on the ability of a number of analytical approaches to make quantitative predictions in supercooled liquids. In this paper, we have only focused on MCT, and we leave for a future publication a more general discussion of the consequences of this finding. Our results also motivate further research to detect more complicated forms of “hidden,” “amorphous,” or “frustrated” order in liquids approaching the glass transition.

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