

## Nonperturbative Effect of Attractive Forces in Viscous Liquids

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We study the role of the attractive intermolecular forces in the viscous regime of a simple glass-forming liquid by using computer simulations. To this end, we compare the structure and the dynamics of a standard Lennard-Jones glass-forming liquid model with and without the attractive tail of the interaction potentials. The viscous slowing down of the two systems is found to be quantitatively and qualitatively different over a broad density range, whereas the static pair correlations remain close. The common assumption that the behavior of dense nonassociated liquids is determined by the short-ranged repulsive part of the intermolecular potentials dramatically breaks down for the relaxation in the viscous liquid regime.

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Differentiating the respective roles of repulsive and attractive intermolecular forces in the properties of fluids and liquids has a long history in statistical mechanics [1]. The so-called “van der Waals picture of liquids” [2,3], i.e., the predominance of the short-ranged repulsive part of the intermolecular potentials in determining the structure of dense nonassociated liquids, has proved very fruitful for predicting the pair correlation functions and the thermodynamics. Although not as thoroughly tested [4–8], it has been useful for the dynamics as well [9].

More recently, this picture, in which the attractive part of the interactions is treated as a mere cohesive background amenable to perturbative treatment, has been transposed to the viscous (supercooled) liquid regime. A number of approaches either suggest or take for granted that the structure and the dynamics of viscous glass-forming liquids are controlled by the short-ranged repulsive forces. Among them are studies based on the mode-coupling theory of glasses [10], the self-consistent phonon theory [11], model potential energy landscapes [12], as well as recent work focusing on the correlations between pressure and energy fluctuations [13,14] and on the density scaling of the relaxation time [15]. Predominance of the short-ranged repulsive forces is also shared by the “jamming scenario,” which postulates that the physics of glasses and glass-forming liquids is controlled by a zero-temperature critical point characteristic of the jamming [16,17] or glass [18] transition of spheres with finite-ranged repulsive interactions, with the longer-ranged attraction considered as a perturbation.

However, and quite surprisingly, the central hypothesis underpinning this large set of ideas has never been directly studied. It therefore appears timely to assess the role of the attractive intermolecular forces in the viscous liquid regime. Our central conclusion is that in the regime that is probed experimentally, attractive forces have little effect

on the structure of the liquid, but affect their dynamics in a strong, likely nonperturbative, way.

In this work, we compare by means of molecular dynamics simulation the structure and the dynamics of a standard model of glass-forming liquid, the Kob-Andersen 80:20 binary Lennard-Jones mixture [19] and its reduction to the purely repulsive part of the pair potentials proposed by Weeks, Chandler, and Andersen (WCA). In the following, the former is denoted by “LJ” and the latter by “WCA.” The interatomic pair potential between species  $\alpha$  and  $\beta$ , with  $\alpha, \beta = A, B$  is given in the two systems by

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

and is zero otherwise, where  $r_{\alpha\beta}^c$  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 simulations are performed in the *NVE* ensemble (after equilibration at a chosen temperature) with  $N = 900$ – $1300$  particles (depending on the density) and with periodic boundary conditions. A broad range of density has been considered with  $\rho$  from 1.1 to 1.8. Lengths, temperatures, and times are given in units of  $\sigma_{AA}$ ,  $\epsilon_{AA}/k_B$ , and  $(m\sigma_{AA}^2/48\epsilon_{AA})^{1/2}$ , respectively. In line with the WCA theory, the two liquid models are compared at the same  $(\rho, T)$  state points. Their pressure then differs, with the attractive interaction roughly providing a temperature independent negative shift.

We first consider the static structure of the liquids as characterized by the pair correlation functions  $g_{\alpha\beta}(r)$ . The pair correlation of the density fluctuations,  $g(r) = \sum_{\alpha\beta} x_{\alpha} x_{\beta} g_{\alpha\beta}(r)$  with  $x_{\alpha}$  the concentration of species  $\alpha$ , is displayed in Fig. 1 for two temperatures at the typical liquid density of 1.2. As anticipated [2], the attractive

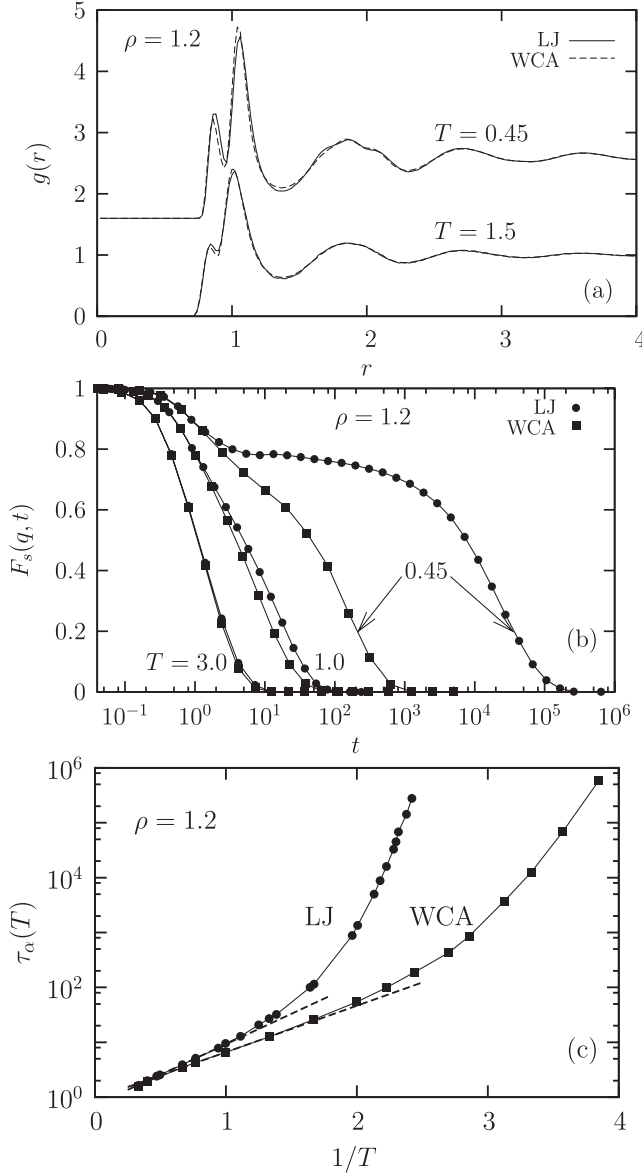


FIG. 1. Comparison between the LJ and its WCA description at the typical liquid density  $\rho = 1.2$  for several temperatures. (a) Static pair correlation functions  $g(r)$  as a function of  $r$ ; (b) Time dependence of the self-intermediate scattering function for the majority component A; (c) Arrhenius plot of the relaxation time  $\tau_\alpha$  defined from  $F_s(q, t = \tau_\alpha) = 1/e$  (the lowest  $T$  is 0.43 for LJ and 0.26 for WCA), with high- $T$  Arrhenius fits shown as dashed lines. Despite similar pair structure, both systems display dramatically different dynamics.

forces play virtually no role in the high- $T$  liquid. The same is found at very high density ( $\rho \gtrsim 1.6$ , not shown here) for all  $T$ 's. We observe that the contribution of attraction remains very small over the whole range of  $(\rho, T)$  under study. Inspection of the partial correlation functions  $g_{\alpha\beta}(r)$  shows the same feature. A detectable effect is observed for the minority component on  $g_{BB}(r)$ , but since  $x_B = 0.2$ , it has little impact on  $g(r)$ .

Turning to the dynamics, we present the data for the time dependence of the self-intermediate scattering function

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

with  $q\sigma_{AA} \approx 7.2$ , which corresponds to the position of the peak of the total static structure factor at  $\rho = 1.2$ . We see that in the high- $T$  liquid [Fig. 1(b)], the agreement between WCA and LJ is not perfect but is quite good (a factor of 2 or less difference in the relaxation time for  $T \gtrsim 1$ ,  $\rho = 1.2$ ). However, the difference between the two systems rapidly increases as one enters the viscous regime and becomes enormous at the lowest accessible temperatures. The relaxation time  $\tau_\alpha$  of the WCA model is then more than 3 orders of magnitude faster than that of the LJ model [see Figs. 1(b) and 1(c)].

This is confirmed by other measures of the slowing down of relaxation. For instance, the empirically determined mode-coupling singularity temperature  $T_c$ , obtained by an algebraic fit of the temperature dependence of  $\tau_\alpha$ , is roughly divided by two when removing the attractive forces. We point out that, although not appreciated before, similar conclusions can be drawn by comparing the results already published in the literature for different Lennard-Jones mixtures [19,20] and for their WCA truncations [21,22].

We find that it is only by going to very high densities that the difference shrinks and the relaxation times of the two systems become more comparable. Yet, even at a density as high as 1.6, i.e., more than 30% above the commonly used density of 1.2, there is almost an order of magnitude difference between the relaxation times of the two systems, and at  $\rho = 1.8$ , relaxation times still differ by 50% at low temperatures, despite the fact that the pair correlation functions essentially coincide at these densities. These observations prove that the dynamics is not uniquely determined by the static pair correlation functions, raising some doubts on the ability of the mode-coupling theory to properly describe the phenomenon.

The above results unambiguously show that the relaxation of the LJ liquid is considerably slowed down by the presence of the attractive forces as the liquid is cooled down in the viscous regime and approaches the glass transition. One may however wonder whether this is a mere quantitative effect that can be accommodated by introducing an effective energy scale that takes into account the mean influence of the attractive part of the potentials by renormalizing the temperature scale [8,15,23]. To test this hypothesis, as well as to represent all of our data for different densities on the same graph, we have fitted the temperature dependence of the relaxation time in the high- $T$  regime to an Arrhenius formula:  $\tau_\alpha \approx \tau_\infty \exp[E_\infty(\rho)/T]$ . This allows us to collapse the data at high  $T$  with a good accuracy and to extract an effective activation energy scale  $E_\infty(\rho)$ . The latter can then be used to compare the relaxation data in the presence and in the

absence of attraction on a renormalized temperature scale  $T/E_\infty(\rho)$  and therefore to test the above hypothesis. No emphasis is put on the physical meaning of this Arrhenius fit, which we take as a convenient and nonsingular representation of the high- $T$  data.

The results are shown in Figs. 2(a) and 2(b) where we plot the logarithm of  $\tau_\alpha$  for LJ and WCA for all densities between 1.1 and 1.8 as a function of the inverse of the scaled temperature,  $E_\infty(\rho)/T$ . By construction, all curves coincide at high (scaled) temperature above some “onset,”

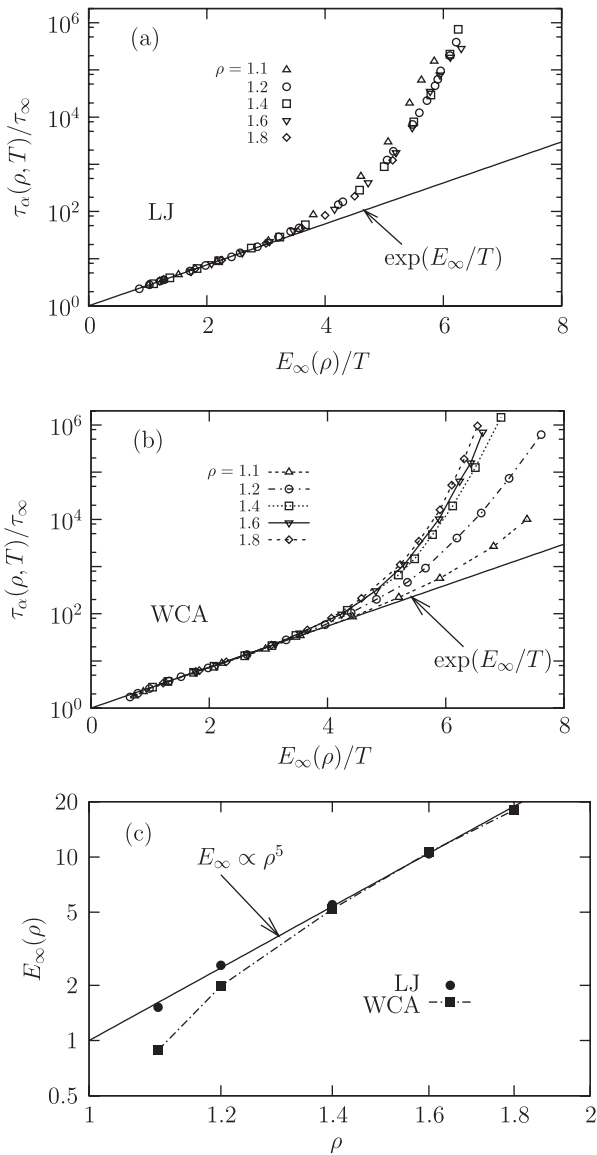


FIG. 2. Rescaling of the relaxation data for the LJ and WCA models over a wide range of densities and temperatures. We use the activation energy scale  $E_\infty(\rho)$  obtained by fitting the high- $T$  data to an Arrhenius formula. (a) Arrhenius plot of the relaxation time for a scaled temperature  $T/E_\infty(\rho)$  for LJ. (b) Same plot for WCA. Note the large change of fragility with density for  $\rho \leq 1.4$ , not seen in the LJ data. (c) Density dependence of the activation energy scale for the two models, with LJ data fitted with a power law.

$T/E_\infty(\rho) \approx 0.3$ , at which the viscous regime roughly starts and departure from simple Arrhenius fit becomes significant. Below this onset temperature, we find that all LJ data essentially collapse onto a master curve (with a small deviation seen for the lowest density of 1.1), as roughly do the WCA data for the three highest densities ( $\rho = 1.4, 1.6, 1.8$ ). The coincidence between LJ and WCA rescaled data is only fair at those densities, and the curves clearly diverge as one lowers the density to reach values more typical of regular supercooled liquids, i.e.,  $\rho = 1.2$  [compare Figs. 2(a) and 2(b)]. The isochoric “fragility” of the WCA model is strongly density-dependent. This is reminiscent of the behavior found in dense fluids of harmonic repulsive spheres [18], but is clearly at variance with the almost constant isochoric fragility of the LJ.

For completeness, we display in Fig. 2(c) the density dependence of  $E_\infty(\rho)$  for the 2 systems in a log-log representation. For LJ, it roughly goes as  $\rho^5$ , in agreement with previous work finding relaxation data collapse with the scaling variable  $\rho^\gamma/T$  with  $\gamma \approx 5$  [15]. The role of repulsive forces in determining the value of  $\gamma$  is discussed in detail in Refs. [13–15].

The viscous slowdowns of the LJ and WCA models are therefore not only quantitatively different at a given density, they are also qualitatively distinct. The density scaling of the relaxation that is empirically found in real glass-forming liquids and polymers [24–27], and in the LJ model as well (see Fig. 2(a) and Refs. [15,24]), is strongly violated when attractive forces are truncated. These findings show that, contrary to expectations, the attractive components of the pair potentials play a crucial role in the viscous liquid regime when approaching the glass transition. A purely repulsive WCA system of course displays a slowing down of relaxation that should end up in glass formation at low enough  $T$ , but some of the characteristics of this slowing down, including the absence of density scaling of the relaxation time, are at odds with the behavior of the full LJ model it is supposed to describe, and of real glass-formers.

Finally, we map out in Fig. 3 the various regimes studied here in a  $(\rho, T)$  phase diagram and discuss the relevance of our findings to real glass formers. On top of the thermodynamic transition lines, we have plotted the empirically determined mode-coupling line,  $T_c(\rho)$ , as an indication of the trend for the (isochronic) glass transition line in the diagram. One can schematically distinguish three regions. Region (I), inside the gas-liquid coexistence curve (or spinodal [28]), can only be accessed by removing the attractive part of the potentials. This is the region that could be controlled by a zero-temperature jamming [16,17] or glass [18] critical point. Region (II) is the experimentally accessible range of glass-forming liquids, for which, typically, the pressure can be varied from 1 bar to 10 kbars with an associated density variation of 20–25%. Finally, region (III) is a high- $T$ , high- $\rho$  regime that is only reachable in computer simulations of model systems. It is only in this region that the role of the attractive forces on both the

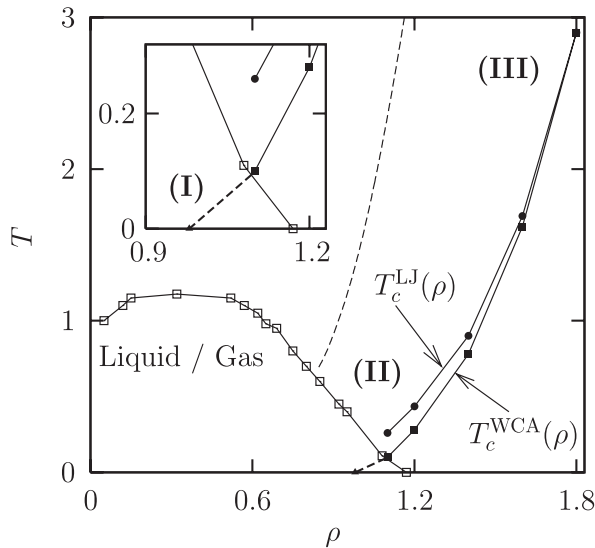


FIG. 3. Phase diagram of the LJ model. The melting line (shown as a dashed line) is for the one-component model [30]. We distinguish 3 regions. (I) is inside the liquid-gas spinodal and is only accessible for WCA: see the zoom in the inset. The extrapolated curve shown as a dotted line ends in a putative zero-temperature singularity [16,18]. (II) is the range corresponding to the experimentally accessible liquid regime, where large differences are found in the dynamics of the two models. (III) is the high- $T$  and high- $\rho$  region only reachable in computer simulations of model systems, in which the role of the attractive forces becomes small or negligible.

statics and the dynamics becomes small and could be treated perturbatively.

The important result obtained in our study is that the dynamics in region (II) at temperatures characteristic of viscous liquid behavior is strongly influenced, and in a highly nontrivial and nonperturbative way, by the attractive forces. It seems therefore unlikely that an extrapolation from either regime (I) or regime (III) could fruitfully describe real glass-forming liquids in region (II). Thus, the common assumption that the behavior of dense non-associated liquids is determined by the short-ranged repulsive part of the intermolecular potentials dramatically breaks down for the dynamics in the viscous liquid regime. A possible explanation goes along the lines already put forward by the promoters of the WCA theory: the effect of the attractive forces is known to be enhanced in the presence of mesoscale heterogeneities in the liquid [29]. It is then tempting to speculate that the effect seen in the viscous regime results from the increasingly collective nature of the relaxation.

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