Chemical Physics 450-451 (2015) 91–94

Contents lists available at ScienceDirect

Chemical Physics

journal homepage: www.elsevier.com/locate/chemphys

A simple diatomic potential that prevents crystallization in supercooled liquids simulations

A.P. Kerasidou [a,b], Y. Mauboussin [b], V. Teboul [a,*]

[a] *Laboratoire de Photonique d'Angers EA 4464, University of Angers, Physics Department, 2 Bd Lavoisier, 49045 Angers, France*
[b] *MOLTECH Anjou, University of Angers, 2 Bd Lavoisier, 49045 Angers, France*

ARTICLE INFO

Article history:
Received 20 November 2014
In final form 11 February 2015
Available online 16 February 2015

Keywords:
Dynamic heterogeneity
Glass-transition
simulation
potential
Crystallisation

ABSTRACT

We study a simple and versatile diatomic potential function coined to prevent crystallization in supercooled liquids. We show that the corresponding liquid does not crystallize even with very long simulation runs at the lowest temperature that we can access with ergodic simulations. The medium displays the usual features of supercooled materials and a non-Arrhenius dependence of the diffusion coefficient and α relaxation time with temperature. We also observe the breakdown of the Stokes–Einstein relation at low temperatures.

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1. Introduction

Supercooled liquids undergo an exponential (Arrhenius) or even larger increase of their viscosity when the temperature decreases. This large modification of the transport properties appear while the structure changes only slightly with temperature. While several theories [1,2] have been proposed to solve that long standing glass-transition problem, it is still open [3,4,1,2,5]. Interestingly while the reasons for the strange behavior of supercooled liquids are still not understood, molecular dynamics simulations [6] reproduce the unexplained phenomena [4,1]. Consequently molecular dynamics simulation is an invaluable tool [6–11] to study the glass-transition problem, and more generally [6,13–16,12,17] for the study of condensed matter physics. Due to the universality of the glass-transition phenomenology [4,1,2,5] one is tempted to chose the simplest existing potential function in order to simplify as much as possible the complexity of the problem. Unfortunately when the potential is too simple, the liquid crystallizes rapidly. Thus one is conducted to search for the simplest potential that prevents crystallization for supercooled liquids simulations while displaying as strongly as possible the dynamical behavior of supercooled liquids. Various potentials [20–25,18,19] have been proposed in that purpose. However some eventually undergo partial crystallization for long runs, while others are not so simple. The most popular potential to date that hinders the crystallization is the Kob-Andersen potential [18,19]. The corresponding liquid is a mixture of two different Lennard-Jones atoms (A and B) with a proportion of 20% of atoms A and 80% of atoms B. If that potential is one of the simplest it also creates an unnecessary increase of the complexity of the problem due to the mixture of atoms. However liquids constituted with only unmixed atoms A or B do crystallize very fast. A simple idea to overcome that problem is to bound the two atoms A and B creating a diatomic molecule which liquid may be expected not to crystallize. Unfortunately after long runs that liquid also crystallizes partially.

In this work we study a simple and relatively versatile potential function, based nonetheless on that idea of two bounded Lennard-Jones atoms which parameters are chosen to prevent crystallization. Due to its simple Lennard-Jones structure we expect that potential to be a good candidate to model the universal physics of molecular liquids. We show that the liquid constituted by these molecules does not crystallize at low temperatures and that it follows the typical behavior of non-Arrhenius supercooled liquids.

2. Calculation

We model the molecules as constituted of two atoms ($i = 1, 2$) that do interact with the following Lennard-Jones potentials: $V_{ij} = 4\epsilon_{ij}((\sigma_{ij}/r)^{12} - (\sigma_{ij}/r)^{6})$ with the parameters: $\epsilon_{11} = \epsilon_{12} = 0.5$ KJ/mol, $\epsilon_{22} = 0.4$ KJ/mol, $\sigma_{11} = \sigma_{12} = 3.45$ Å and $\sigma_{22} = 3.28$ Å. Note that as in the Kob-Andersen model [18,19] we do not use the usual additive mixing rules [6] for Lennard-Jones potentials. We make that choice of non-additive mixing rules as it has the property to

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* Corresponding author. Tel.: +33 241735004.
E-mail address: victor.teboul@univ-angers.fr (V. Teboul).

http://dx.doi.org/10.1016/j.chemphys.2015.02.009
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hinder the crystallization and the formation of plastic crystal phases [26–28,30,31,29,32]. We use the mass of Argon for each atom of the linear host molecule that we rigidly bonded fixing the interatomic distance to $d = 1.73$ Å. The reduced shape [30,31] of our dumbbell molecule is $L^* = d/\sigma = 0.5$ a value somehow larger than the limit $L^* = 0.4$ below which plastic phases are usually created [30,31]. With these parameters the liquid does not crystallize even during long run simulations. The simulations are first equilibrated during 20–100 ns depending on the temperature, then we perform the production run. However a few long runs of 400 ns each, have also been realized at low temperature ($T = 40$ K) with a smaller simulation box containing 500 molecules only and we did not find any sign of crystallization. We use the Gear algorithm with the quaternion method [6] to solve the equations of motions with a time step $\Delta t = 10^{-15}$ s. The temperature is controlled using a Berendsen thermostat [33]. The density is set constant at $\rho = 2.24 \text{g/cm}^3$. We use in our calculations a cubic simulation box that contains $N = 2688$ molecules and has a length $L = 53$ Å. The model has the interesting property to be versatile allowing modifications without crystallizing. For example one can easily change the mass of the atoms leading to different densities or change the interatomic distance d.

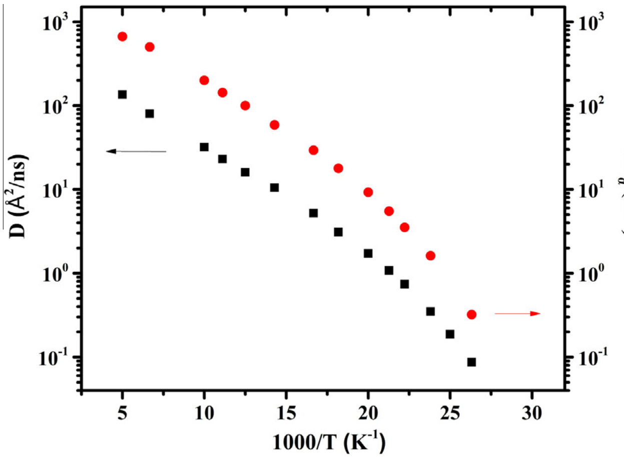

Fig. 2. Diffusion coefficient (black squares) and inverse of the α relaxation time (red circles) evolution with temperature. The Figure shows an evolution faster than a pure exponential. That evolution called super-Arrhenius is typical of molecular supercooled liquids.(For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3. Results and discussion

To verify that there is no crystallization in our liquid, we plot in Fig. 1 the radial distribution function (RDF) for various temperatures ranging from above the melting temperature to a deep supercooled liquid.

The radial distribution function $g(r)$ represents the distribution probability to find a molecule a distance r apart from another molecule. We see on the Figure that the RDF does not change much when the temperature decreases from above the melting temperature down to the lowest accessible temperature with our simulations ($T = 38$ K). As the temperature decreases, the peaks increase in size, but we do not see any modification of the maxima and minima locations that would have been the signature of a modification of the structure. We do not see ever any sharp peak signalling a partial crystallization of the liquid. Moreover the structure appears to be very simple, quite like the structure of a simple monatomic liquid. The main difference is a small shoulder that we observe in the first peak of the RDF. This shoulder appears due to the difference between the Lennard-Jones potentials of the two atoms constituting the molecule.

We will now study the dynamic properties of the liquid. The diffusion coefficient as well as the α relaxation time in Fig. 2 display a super-Arrhenius evolution with temperature. If the diffusive motions are thermally activated processes we may write: $D = D_0.e^{-E_a/k_B T}$, where E_a is the activation energy to overpass for the molecule to diffuse. A super-Arrhenius evolution implies that the activation energy E_a is increasing when the temperature decreases and for that reason that behavior has been associated in the past with the emergence of cooperativity. This super-Arrhenius behavior also show that our liquid is a "fragile" liquid in Angell's classification [34,35]. This comportment is typical of molecular liquids, suggesting that our model is well suited for molecular liquids. We also observe that the α relaxation time evolves more rapidly than the diffusion coefficient at low temperatures. This result suggests a breakdown of the Stokes–Einstein relation [36]. Note that the diffusion coefficient D decreases continuously with the temperature showing no sign of a sharp drop of D induced by a crystallization process.

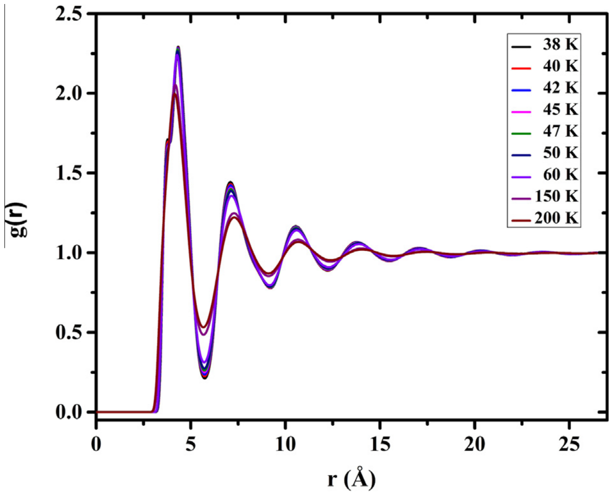

Fig. 1. Radial distribution function $g(r)$ between the molecules center of masses for various temperatures. The structure does not change much even at low temperature. We do not see any peak signalling a partial crystallization at low temperatures. Below 150 K the liquid is supercooled.

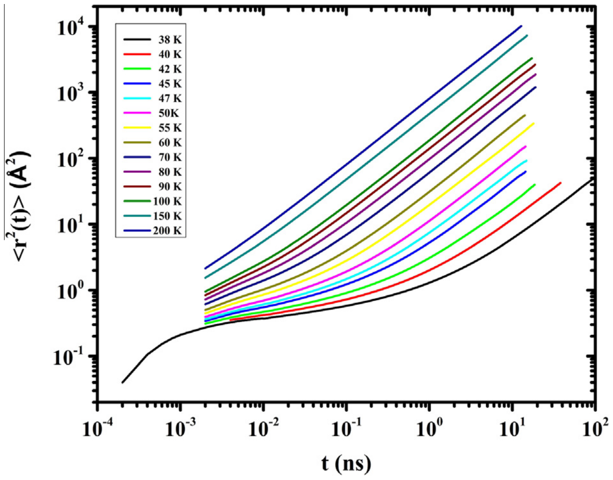

Fig. 3. Mean square displacement of the molecules center of masses plotted for various temperatures. The curves display a plateau typical of the supercooled state and that disappears above the melting temperature $T_m \approx 150K$.

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