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Can models of charged rods show features of undercooled liquids?

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Abstract

We have performed molecular dynamic simulations of linear charged particle models. They are defined by rods with discrete charges at the ends. Intermolecular interactions are described by a coulombic term plus a Kihara potential for the rest of interactions. Our simulations were carried out for low and high charged systems either at thermodynamic states corresponding to the liquid branch of vapor–liquid equilibrium curve of non-charged rods or at supercritical temperatures of the non-charged systems. Our results show that rods with null or small discrete charge behave as normal liquids: the viscosity increases with rod length and they present short range velocity self-correlation function (VSCF). However, for medium and large discrete charges VSCF shows a very long range tail and the apparent viscosity increases by several orders of magnitude with a non-Arrhenius dependence with temperature. In some cases a transition from Arrhenius to non-Arrhenius behavior for medium charges is observed. Our results strongly suggest that systems behave as normal liquids when the rods have null or small charges and show undercooled liquid behavior for larger discrete charges at low temperatures.

Keywords: Correlation functions; Non-Arrhenius viscosity; Diffusion coefficient

1. Introduction

The study of the glassy state from a microscopic point of view has experienced a spectacular expansion over the last few years [1]. The classification of glasses as strong and fragile glasses according to the variation of their viscosity with temperature has supposed a landmark in the study of these systems [2]. During the last few years a number of systems composed by different substances, probably more than in all the preceding centuries, have been identified as glass formers. These systems do not freeze normally at the melting point, suffering a first order phase transition as the normal liquids do. On the contrary, they remain as liquids at temperatures lower than the melting point. Viscosity of undercooled liquids changes by several orders of magnitude in a range of a few Kelvin. In these cases, rotation and vibration degrees of freedom are only partially frozen showing an energy landscape with a huge number of accessible wells of different depth. When temperature decreases even lower the freezing points, the number of accessible depths dramatically decreases and the diffusion coefficients also abnormally decrease. It is in these circumstances that the well-known Stokes–Einstein relation stops fulfilling. Not only these features but also a few else are well enumerated by Casalini et al. [3] to define an undercooled liquid. The most extensively studied undercooled liquid in the last few years is undoubtedly water [4], not only due to its own relevance but also because it seems to show polyamorphism [5], including a second critical point at temperatures well below the normal freezing point. This polyamorphism is a new peculiarity of a liquid with a number of well-known peculiarities [6]. Furthermore, polymers are the typical examples of undercooled liquids but they present polydispersity or, in molecular terms, they are a mixture of molecules of different chain lengths. We restricted ourselves in this work to monodisperse substances where polymers are explicitly excluded but additional examples of organic [7,8] and inorganic [9] relevant molecules are known. In particular, it is well known that hydrocarbons or closely related compounds can remain during centuries forming asphalts or shoe-polish lakes as La Brea Lake not far from Los Angeles or Bermúdez Lake in Venezuela. Moreover, in marine spills, the appearance of "chapapote" (from nahuatl Chapopotl, asphalt) is a relevant environmental problem currently. The behavior of these undercooled liquids is far from being well understood from a molecular point of view. The

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main goal of this paper is to show how a simple model as an overall neutral rod with a heterogeneous distribution of electric charge can show the behavior of a glassy system. The systems presented here can be modeled more easily than water and their properties are crucial in the case of marine spills. We found that the behavior of the non-charged rods of different lengths is as expected showing a typical vapor–liquid equilibrium as obtained by Gibbs ensemble Monte Carlo (GEMC) simulations. Furthermore, we have carried out Molecular Dynamics simulations and we show in this paper that the transport properties of non-charged rods at a given thermodynamic state also show the expected behavior of transport properties (viscosity, η, steadily increasing with the length of the rod). Nevertheless, it should be noted that a (cubatic) glass phase was found for uncharged rods of intermediate aspect ratio [10]. The results are markedly different when considering rods with charges on the extremes. Several previous results [11–13] have been reported for rods with charges on the extremes but, as far as we are aware, these results refer only to thermodynamic or structural aspects. In this paper, we find that models with small charges behave in a similar way as non-charged systems but for medium and high charges the dynamic behavior changes dramatically. Correlation functions show a very long range tail, corresponding to abnormal values of diffusion coefficient, D, and viscosity, η. In some cases, abnormal behavior persists even at temperatures well above the critical temperature corresponding to non-charged system. In other cases, typically mean charge values, a transition from a high viscosity liquid to a normal liquid is observed when the temperature increases. We have shown [14] that in some cases, rods with separated even charges can be compared with dipoles but the appearance of a glassy system for α-chloroalkanes or 1-n-alcohols has not been observed, as far as we are aware, even for Kihara long rods with a centered point dipole [15]. On the other hand, peptides close to their isoelectric point, namely with an important proportion of zwitterions do show features of a glassy state and, consequently are difficult to crystallize [16]. We thought that our model can be particularly useful for these systems as well as for marine spills with an important proportion of highly charged metallic cations, as different species of Ni(II) or V(V). These cations are highly polarizing and may induce a dipole on the oil by creating an intramolecular charge separation. This induced dipole increases with the polarizability, or roughly with the molecular volume [17] or the chain length.

2. Model and simulation details

Our model consists of rods interacting through dispersion forces depending only on the shortest distance between a pair of rods. Moreover, a first net charge is located on one of the extremes of the rod and a second charge – equal in absolute value but opposite in sign – on the other extreme. This model is a typical coarse graining model and we have chosen the so-called Kihara intermolecular potential [18,19] providing some realistic characteristics to the non-electrostatic part

$$u_{ij}^{K} = 4\varepsilon\left[\left(\frac{\sigma}{\rho_{ij}}\right)^{12} - \left(\frac{\sigma}{\rho_{ij}}\right)^{6}\right] \tag{1}$$

where ε and σ are potential parameters and ρ_{ij} is the shortest distance between linear cores modeling molecule i and molecule j (see Fig. 1). The shortest distance depends on

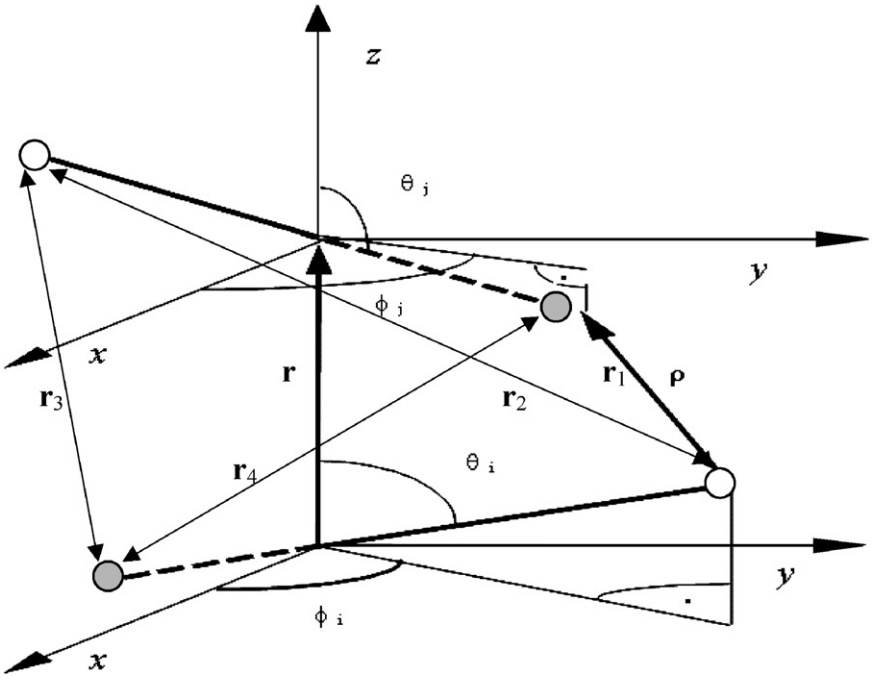

Fig. 1. The model used in this work showing the shortest distance between rods and the position of the charges (small balls in the figure). Gray and white balls correspond to charges of different sign.