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Q1 The Frenkel line and isotope effect

Q2 Yu.D. Fomin^{a,b,*}, V.N. Ryzhov^{a,b}, E.N. Tsiok^a, V.V. Brazhkin^a, K. Trachenko^c

^a Institute for High Pressure Physics RAS, 142190, Kaluzhskoe shosse 14, Troitsk, Moscow, Russia

^b Moscow Institute for Physics and Technology, 141700, Institutskii per. 9, Dolgoprudny, Moscow region, Russia

^c School of Physics and Astronomy Queen Mary University of London, Mile End Road, London E1 4NS, United Kingdom

HIGHLIGHTS

- Liquids can have two dynamically different regimes separated by a crossover line.
- The line of dynamical crossover in isotopic mixtures is studied.
- The partial crossover lines strongly depend on the isotopic composition.
- The total crossover line demonstrates very weak dependence on the isotopic composition.

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ABSTRACT

It has been recently proposed that supercritical fluids experience a crossover between two different regimes of the particle dynamics. The crossover takes place at the Frenkel line which can be defined from vanishing of oscillations of the velocity autocorrelation functions (vacfs). Here, we present a novel detailed analysis of vacfs of binary isotopic mixtures of Lennard-Jones and Soft Spheres particles and consider temperature dependence of vacfs of individual components as well as mixtures. We show that partial vacfs can be very different: for the mass ratio of about 2, the temperature at which the oscillatory behavior of vacf vanishes differs eightfold. Notably, oscillatory behavior of vacfs of the whole mixture vanishes at about the same temperature as in the one-component fluid. We conclude that the criterion to locate the Frenkel line on the basis of vacfs is general and applies to mixtures, reflecting more fundamental changes of system dynamics such as the disappearance of transverse mode from the excitation spectrum.

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1. Introduction

Supercritical fluids are of great importance for both fundamental research and technological applications, attracting substantial attention of scientific community worldwide. Several empirical proposals were aimed at finding a way to distinguish between gas-like and liquid-like states above the critical point. A physically meaningful approach to do so was discussed in our recent publications [1–3]. The approach is based on the idea that even though the system is above the critical point, the temperature- or pressure-induced changes of microscopic dynamics are well-defined. Based on these changes one can define two regimes of supercritical fluid: rigid liquid and dense gas (or non-rigid fluid) ones separated by a crossover line which it was proposed to call Frenkel line [1–3].

Several methods to locate the Frenkel line were proposed. Applying these methods, we calculated the Frenkel lines of several model systems such as Lennard-Jones liquid (LJ), soft spheres liquid (SSp) [1–3] and several realistic liquids: liquid

* Corresponding author at: Institute for High Pressure Physics RAS, 142190, Kaluzhskoe shosse 14, Troitsk, Moscow, Russia.
E-mail address: fomin314@gmail.com (Yu.D. Fomin).

iron [4], carbon dioxide CO₂ [5] and water [6]. Other groups reported the Frenkel lines in molecular hydrogen [7], methane, water and carbon dioxide [8]. It was found that the Frenkel lines of different substances demonstrate some similarities. The important common feature is that at high pressure, the Frenkel line is almost parallel to the melting line in double logarithmic coordinates.

The Frenkel line is affected by details of the particular system, including interatomic potential, chemical composition and so on. It is currently not clear how system-specific microscopic properties affect the Frenkel line. Most conveniently, the Frenkel line is defined by the velocity autocorrelation function (vacf): $Z(t) = \frac{1}{3N} \langle \sum_{i=1}^N \frac{\mathbf{V}_i(t)\mathbf{V}_i(0)}{V_i(0)^2} \rangle$ ($\mathbf{V}_i(t)$ is an i th particle velocity at time t and the sum is over $3N$ velocity components in the system). In a solid, vacf demonstrates long-living oscillations, corresponding to periodic changes of the direction of velocity of a particle, i.e. oscillations around a quasi-equilibrium point. In a gas, vacf monotonically decays to zero. Vacfs of liquids have an intermediate behavior: they demonstrate several oscillations and then decay to zero. As early as in 1970-s it was noticed that even for the simple systems like the inverse power potential $U(r) = \varepsilon \left(\frac{\sigma}{r}\right)^n$ (soft spheres), vacfs of the fluid can have qualitatively different behavior [9]. If one considers vacfs of soft spheres along $\gamma = \text{const}$ ($\gamma = \rho\sigma^3 \left(\frac{\varepsilon}{k_B T}\right)^{3/n}$), the vacf crosses zero close to the melting line, implying that particles quickly change the direction of their motion. On heating, the vacf increases above zero but preserves the oscillatory behavior. It means that although particle velocities do not change direction, the acceleration does. Low temperature liquids are often described in terms of energy landscape: the system is located in a minima of free energy and from time to time it jumps into another minimum. As temperature increases the minima decrease and finally disappear. Therefore the system becomes free to move from one state into another one. One can relate the change in acceleration sign to the energy landscape of the liquid. If a system is in a minimum and tries to escape from it a returning force appears. It is this force which makes the acceleration negative. On further heating, the behavior of the vacf starts to decay to zero monotonically as in a gas which corresponds to effective disappearance of minima of the energy landscape. The investigations of vacf of fluids and their relation to particles dynamics were continued in later publications [10,11].

Therefore, the crossover from oscillating to monotonically decaying vacf serves as a convenient mathematical criterion to detect the change of microscopic dynamics of the supercritical system from liquid-like to gas-like and locate the Frenkel line [3]. We have found that the vacf criterion agrees very well with the condition $c_v = 2k_B$, supporting the proposal in the first papers on the Frenkel line [1,2]. The agreement is not coincidental: the loss of the oscillatory behavior implies $\tau \approx \tau_{\text{max}}$, where τ is liquid relaxation time, the time between consecutive particle jumps at one point in space [12] and τ_{max} is the minimal period of transverse vibrations. Coupled with the Frenkel theory that liquids support transverse modes with frequency $\omega > \frac{1}{\tau}$, this means that the system cannot support transverse modes when $\tau \approx \tau_{\text{max}}$ at the Frenkel line [13]. According to the phonon theory of liquid thermodynamics, the system with only one longitudinal mode has $c_v = 2k_B$ [14]. On further temperature increase above the Frenkel line, the system enters the regime of gas-like dynamics, and c_v undergoes a crossover to a much slower decrease related to the evolution of the remaining longitudinal mode [15,16].

The two criteria to locate the Frenkel line on the basis of vacf and c_v were checked for several systems, including LJ, soft spheres [3] and liquid iron [4], showing excellent agreement.

Until now, only one-component fluids have been considered (molecular liquids in Ref. [8] were simulated with the rigid-body interatomic potential and with fixed ratios of atomic masses). One expects to find more complex behavior in multi-component systems. The simplest example of a multi-component liquid is a binary mixture of isotopes, particles of different types, which we refer to as particles A and B having the same interaction parameters but different masses.

The isotope effects were discussed in some previous studies. However, to the best of our knowledge all these studies were concerned with the relationship between the isotope effect and diffusion coefficient, the integral of vacf, but not the vacf itself. At the same time it is of common knowledge that vacfs are among the main dynamical characteristics of a fluid therefore they are of special interest.

Among the first simulations of the mass dependence of diffusion coefficients is the Ref. [17]. This article studies the diffusion coefficient of a single hard sphere in the solvent of hard spheres of larger mass. The results were compared with Enskog theory [18] predictions and large deviations were detected. A similar study with LJ fluid was performed in Ref. [19]. Here an LJ particle of different size and interaction parameters is introduced in the solvent of other LJ particles, i.e. the system is not isotopic. However, only one density and few low temperatures were studied. In results the authors found only small influence of the solute particle on the vacfs and diffusion coefficient of the system.

A detailed study of the isotope effect on the diffusion coefficient was performed in Ref. [20]. Considering three mass ratios and using molecular dynamics simulations of the binary Lennard-Jones (LJ) system, the study concluded that while the diffusion coefficients of light and heavy particles are close to each other, their vacfs are very different, the result partially addressed by the memory function formalism. However, the study was performed at low temperature only so that the disappearance of the oscillatory behavior was not observed. A related study was performed in Ref. [21] where a binary mixtures of isotopes with masses $m_A = m + \Delta m$ and $m_B = m - \Delta m$ was studied with different Δm but constant total mass. Focusing on the diffusion coefficient at low temperature, the authors reported results similar to Ref. [20], adding that the vacf of lighter particles (as well as total vacf) show oscillatory behavior whereas the vacf of heavier particles decays monotonically.

The focus of previous studies was on the diffusion coefficient rather than vacf and its behavior. To the best of our knowledge, there has been no systematic study of vacfs in isotopic mixtures.

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