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Thermodynamics and dynamics of the hard-sphere system: From stable to metastable states

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ABSTRACT

A set of three different scaling laws is investigated, which are devoted to link the transport properties, i.e. diffusion coefficient, shear viscosity, bulk viscosity and thermal conductivity, to the thermodynamic properties for the athermal hard-sphere system, over the wider range of packing fraction covering the stable and metastable regimes. Except for the thermal conductivity, the Rosenfeld (1999) [15] relation is found to be applicable to the stable states while the Adam and Gibbs (1965) [24] relation holds well for the metastable states. In contrast, the modified Cohen and Turnbull (1959) [25] relation proposed here gives sound support for a universal scaling law connecting the dynamic and thermodynamic properties, over the domain of packing fraction including the stable and metastable states. In particular, it is found that the most relevant control parameter is not the excess entropy, but the logarithm derivative of the excess entropy with respect to the packing fraction. In the same context, the Stokes–Einstein relation between the diffusion coefficient and the shear viscosity is also examined. The possible violation of the Stokes–Einstein relation is investigated over a large domain of packing fractions.

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1. Introduction

The hard-sphere system has a prominent position in the study of real fluids. Specifically, equations of state for fluids may be based upon the assumption that, in the limit of high temperature, the real fluids behavior approaches that of hard spheres. For a long time, the equation of state (EOS) has been the object of many analytical [1–3] and simulation [4,5] studies, the last one being based on the chemical potential route [6]. However, the Carnahan and Starling [7] EOS seems to be the most accurate with a remarkable degree of simplicity.

The hard-sphere (HS) system constitutes also the simplest model to tackle a variety of specific issues such as the mathematics of disordered jammed packing [8] or the phase transitions in condensed matter physics [9]. When crystallization is avoided owing to a densification sufficiently rapid of the system, the hard spheres at thermal equilibrium are less and less mobile, and eventually exhibit a glassy behavior at large volume fraction, in analogy with the glass transition of molecular liquids. For large packing fractions, the system is not globally ergodic over the entire configuration space, but it is still possible to generate a metastable extension of the EOS for the HS system beyond the freezing density by considering properties of local minima of a multidimensional potential function within the inherent structure formalism [10]. The movements of the hard spheres are much like those of a vibrating box of ball bearings. If the packing fraction is not too high, each particle can wiggle. But when the packing fraction is high enough, the space available to each particle is constricted, and any significant displacement of one particle must be accompanied by rearrangements of several neighboring particles.

While the thermodynamics of the HS system is well understood for a fairly long time in the context of various statistical mechanics theories [11–13], the transport properties, i.e. self-diffusion coefficient, viscosity, thermal conductivity, are less amenable to accurate theoretical calculation and require intense molecular dynamics computations. Owing to a natural extension of the Boltzmann equation devoted to diluted gas, the Enskog theory provided the first prediction of the transport properties of the HS system. After successive improvements, the Enskog theory to account for the effect of density has also been widely used as a basis for predicting the transport properties of real fluids.

A first attempt to find a semiempirical relation between dynamics and thermodynamics of strongly coupled simple fluids has been probably achieved by Rosenfeld [14], by establishing a correspondence between the transport coefficients and the excess entropy. Later the work has been extended to moderate and dilute fluids, making general predictions about transport properties in agreement

with simulation results [15]. Such a point of view has also been adopted to test this scaling law for the diffusion coefficient of silver-ion in the solid-state ionic conductor for α-AgI [16] and for the self-diffusion coefficient in dense fluid Ar [17] and simple liquid metals [18,19] as well. In the same spirit, we proposed a relation between the diffusion coefficient and the excess entropy for the HS system above the freezing transition, i.e. for low values of the packing fraction [20].

However, the excess entropy seems to lose relevance for low temperatures, and it does not generally correlate with transport properties below the freezing transition [10]. As a result, the excess entropy cannot provide a comprehensive description of metastable-state diffusivity. In contrast, experimental support for the prediction of the dynamic properties near the glass transition reveals a quantitative link between the transport properties and the configurational entropy in supercooled real liquids [21,22], so that liquid diffusion seems to be a process dominated by thermodynamic factors, even if attempts to correlate kinetic properties with the thermodynamic behavior have been controversial, at least in molecular liquids [23]. For the purpose, the Adam–Gibbs theory [24] of structural relaxation is often used, which suggests a link between equilibrium thermodynamics and diverging times scale, i.e. transport properties, when the configurational entropy is equal to zero. Up to then, the entropy Adam–Gibbs theory seems to provide a better showing than the free-volume theory developed by Cohen and Turnbull [25], which has been widely used in the case of polymers.

In this article, we prolong our study [20] on the HS system towards the metastable states with the Torquato [26] equation of state. Since the Rosenfeld and Adam–Gibbs relations are capable of describing the self-diffusion coefficient for many liquids in the stable and metastable states, respectively, it is of interest to ask whether the two relations contain the same thermodynamic information and if Rosenfeld's relation can be used as an alternative to the Adam–Gibbs relation. At the same time, we re-investigate the Cohen–Turnbull theory in order to correlate the transport coefficients with the thermodynamic behavior of the HS system.

This paper is organized as follows. In Section 2, the main results of thermodynamics are presented, i.e. pressure and entropy of the HS system around the freezing density. Section 3 briefly resumes the Enskog expressions for the transport coefficients of the HS system. Section 4 contains a comparison of the scaling relations proposed by Rosenfeld and by Adam and Gibbs for setting the correlation between the transport properties and thermodynamics of the HS system. On the other hand, recasting the free volume Cohen–Turnbull theory in a more transparent form, we derive a new semiempirical relation linking the transport coefficients to the compressibility factor Z instead of the excess entropy, which is competitive with the two other relations to describe the dynamics of the HS system, in stable and metastable regimes. Surprisingly, it results from it that the logarithm derivative of the excess entropy with respect to the packing fraction is found to be the most relevant quantity for checking the diffusive displacement. Lastly, the possible violation of the Stokes–Einstein relation – combining the diffusion coefficient with the shear viscosity – is investigated for the stable and metastable states of HS system.

2. Thermodynamics of the hard-sphere system

The HS system corresponds to a collection of N particles, of diameter σ, contained in the volume V and interacting by means of the potential $u(r)$ equals to ∞, if $r < \sigma$, and to 0, if $r > \sigma$. The traditional dimensionless measure of the density $\rho(= N/V)$ is the packing fraction η, defined as the fraction of the total volume occupied by the spheres and whose the expression is:

$$\eta = \frac{\pi}{6}\rho\sigma^3. \tag{1}$$

An important quantity of the HS system is the pair correlation function $g(r;\eta)$, which is proportional to the conditional probability of finding a particle at position r' given that another particle is located at position r, under the condition that $g(r;\eta) = 0$ if $r < \sigma$. Thus, the thermodynamic properties are calculated as integrals involving the pair correlation function $g(r;\eta)$ and the pair potential $u(r)$. As an example, the statistical theory provides the expressions for the pressure p and the internal energy E in the following forms:

$$p = \frac{\rho}{\beta} - \frac{2\pi\rho^2}{3}\int_0^\infty g(r;\eta)\frac{du}{dr}r^3 dr \tag{2}$$

and

$$E = \frac{3N}{2\beta} + 2\pi\rho N \int_0^\infty g(r;\eta)u(r)r^2 dr, \tag{3}$$

with $\beta = 1/k_B T$, where k_B is the Boltzmann constant and T the temperature. Given the definitions of the pair potential $u(r)$ and the pair correlation function $g(r;\eta)$, the interaction energy of the HS system is equal to zero. On the other hand, since the hard spheres in liquid state are large enough, there is no thermal motion in the system, which is completely driven by the entropy. Therefore the temperature is irrelevant and the thermodynamic properties are fully controlled by the packing fraction η.

The most notable achievement of simulation computations has been to clarify the circumstances of freezing under compression, from small to large packing fractions. As pointed out [4,5], the HS liquid freezes at the packing fraction $\eta_f \simeq 0.494$ and the solid melts at the packing fraction $\eta_m \simeq 0.545$. Besides, computer simulations have shown unambiguously that the liquid–solid transition occurs spontaneously, apparently at random, over an interval of confusion $[\eta_f; \eta_m]$, in such way that it is not possible to have two states simultaneously in equilibrium on the liquid and solid branches. For packing fraction varying from zero to η_f, the thermodynamically stable phase is a liquid. Increasing the packing fraction beyond η_f results in an athermal first-order phase transition to a solid branch that begins at the melting point η_m and ends at the close-packed fcc value $\eta_{fcc} = \frac{\pi\sqrt{2}}{6} = 0.7405$, which is a jammed packing where each particle is in contact with 12 others.

If the Carnahan–Starling (CS) equation of state [7] is chosen to predict the pressure of the liquid branch of HS system – which has some merits in terms of the virial series and agrees very well with the results deduced by simulation –, Eq. (2) is reduced to:

$$\frac{\beta p^{(CS)}}{\rho} = 1 + 4\eta\frac{(1 - \eta/2)}{(1 - \eta)^3}, \tag{4}$$

where $\frac{(1-\eta/2)}{(1-\eta)^3}$ represents the pair correlation function at contact $g(\sigma;\eta)$. The change of entropy in the liquid state can easily be calculated by integration of the pressure with respect to the density using the following thermodynamic relation, which links the excess entropy to the pressure:

$$\frac{S_{ex}}{Nk_B} = -\int_0^\eta \left[\frac{\beta p}{\rho} - 1\right]\frac{d\eta}{\eta}. \tag{5}$$

From the CS EOS, the excess entropy along the liquid branch reads:

$$\frac{S_{ex}^{(CS)}}{Nk_B} = -\frac{4\eta - 3\eta^2}{(1 - \eta)^2}. \tag{6}$$

Since the HS system tends to an ideal gas in the limit of low packing fraction, the absolute entropy of the HS system in liquid state is:

$$\frac{S^{(CS)}}{Nk_B} = \frac{S_{id}}{Nk_B} + \frac{S_{ex}^{(CS)}}{Nk_B}, \tag{7}$$