



Liquid-like and gas-like features of a simple fluid: An insight from theory and simulation

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

^a Institute for High Pressure Physics, Russian Academy of Sciences, Troitsk 108840, Moscow, Russia

^b Moscow Institute of Physics and Technology, Dolgoprudny, Moscow Region, 141700, Russia

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

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ABSTRACT

A soft-sphere system is one of the simplest and most studied models of many-body problems. In contrast to real substances, it does not have a cohesive state and boiling line. For this reason, the fluid phase has been considered to be the same everywhere on the phase diagram with no difference between the gas and liquid phase. Here, we show that the soft-sphere fluid can in fact be demarcated into two states with liquid-like and gas-like properties even though these states are not separated by a thermodynamic phase transition. We find that particle dynamics and excitation spectra are qualitatively different in the two states. This difference applies to other system properties such as viscosity, diffusion and speed of sound. We consider different repulsion exponents of the soft-sphere system as well as the limiting case of the hard-sphere system and comment on their implications for demarcating the fluid phase into liquid-like and gas-like states.

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1. Introduction

A common feature of a phase diagram is the liquid and gaseous states separated by the first-order phase transition boiling line. Although liquid and gas states have the same symmetry, they transform into each other via the first order phase transition. At the same time liquid can be transformed into the gas (or vice versa) without phase transition if one constructs a path above the critical point. Since there is no phase transition along such a path one cannot clearly state when the system is still liquid and when it is already gas. However, many features of liquids looks rather different from those of gas. Because of this one can often see in the literature such terms as “liquid-like” and “gas-like”. For example, the velocity autocorrelation function (VAF) of gases demonstrates monotonous decay to zero while VAF of liquids make one or two oscillations around zero before the decay [1]. Another typical feature which demonstrates qualitatively different behavior in liquids and gases is shear viscosity. The shear viscosity of liquids decreases with temperature while the shear viscosity of gases increases. This effect is related to the fact that the viscosity of liquids is dominated by the interaction of the particles whilst the behavior of the viscosity of the gases is determined by the kinetic term [2]. Interestingly, it leads to rather complex non-monotonous character of the lines of constant viscosity on density–temperature or pressure–temperature planes [3]. Such criteria allow to state if the system in particular pressure–temperature point is liquid-like or gas-like even if there is no phase transition. However, different quantities can give the location of the crossover point at different pressures and temperatures. In the present paper we review several features of the fluids which are often referred as liquid-like or gas-like and compare the results. Basing on this comparison we discuss which of these features can be used as an evincive criterion of a crossover between liquid-like and gas-like states when no phase transition is observed.

* Corresponding author at: Institute for High Pressure Physics, Russian Academy of Sciences, Troitsk 108840, Moscow, Russia.
E-mail address: fomin314@gmail.com (Yu.D. Fomin).

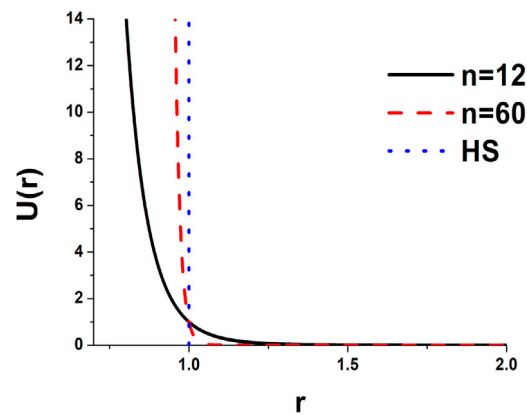


Fig. 1. Potentials considered in the present work: soft spheres with $n = 12$ and 60 and hard spheres.

Here we use a “soft-sphere” (SSp) system. This is a system which consists of the particles with repulsive interaction $U(r) \propto \frac{1}{r^n}$ which gives no cohesion between the particles. The system occupies a finite volume under positive pressure only, and has a simple phase diagram. At high pressure and low temperature, the SSp system is the fcc and bcc crystal for $n > 6$ and $n < 6$, respectively [4,5]. The crystal melts into the fluid phase which is the second and the last phase in this system: no boiling line and hence no difference between the gas and the liquid exist.

The SSp system is used to model and understand several interesting states of matter such as granular media, colloids and dust plasma where no cohesive forces operate. The system has been widely used to model fluids and, together with the hard-sphere system which is the limit of the SSp system for large n , is perhaps one of the best studied, simplest and convenient systems used in computer simulations [1].

The SSp system above the melting line is formally a gas because it is an unbound state at zero pressure (the free energy as a function of volume has no minimum). For this reason, the melted SSp system was always considered as homogeneous with respect to external pressure and temperature. Any analogue of the liquid–gas transition or existence of states with liquid-like or gas-like properties was deemed impossible. However, this system does demonstrate some liquid-like and gas-like features, for example, the shear viscosity of the system decreases with temperature at low temperatures and increases at high ones [2]. It results in a contradiction to be solved in the present paper.

The boiling line and liquid–gas transition exists in most known systems, so the SSp system is rather an interesting and informative exception. However, the matter above the critical point is thought to exist in one state, often referred to as a supercritical fluid. Similarly to the SSp system, no differences can be made between the liquid and the gas in the supercritical state. However, several proposals challenged this view including some recent ideas of how to demarcate the supercritical state into liquid-like and gas-like states, as discussed in more detail below [6–19]. This included the SSp system using the generalized collective mode approach [20]. In this paper, we propose that similarly to the supercritical state, the fluid SSp state can be separated into liquid-like and gas-like states in terms of system properties.

Several previous ideas explored ways in which the supercritical state can be divided into states with different properties. These include the Fisher–Widom line separating different regimes of decay of structural correlations [6,7], several versions of percolation lines through conditional bonds or particles [8,9] and various ways of “thermodynamic” continuation of the boiling line such as the Widom line [10–12]. These approaches have certain limitations. For example, the Fisher–Widom line exists in the stability region of the liquid phase only for low-dimensional model systems only. Percolation lines for realistic fluids can be defined only conditionally. The position of the line of maxima of the correlation length, the Widom line, and the corresponding extrema of various thermodynamic quantities (e.g., specific heat, compressibility, thermal expansion coefficient) depend on the path on the phase diagram. Furthermore, the Widom line exists only near the critical point [11,12,21,22]. Interestingly, no Widom line exists in the SSp fluid because it has no boiling line and thermodynamic anomalies.

On the experimental side, it was found that several features of the dynamic structure factor change qualitatively at pressures several orders of magnitude higher than the critical pressure [13–15]. In addition to dynamical properties, medium-range order structure was found to undergo a crossover at pressure deep in the supercritical region, 250 times the critical pressure [23].

Recently, the concept of the Frenkel line (FL) separating two states of supercritical matter with qualitatively different properties was proposed [16–19,24]. Particles oscillate around quasi-equilibrium positions during time τ , liquid relaxation time, and undergo diffusive jumps between oscillations [25]. The main idea of the FL lies in recognizing that the separation into solid-like oscillatory and gas-like diffusive behavior applies equally to supercritical fluids as it does to subcritical fluids. One can then consider how particle dynamics changes in response to pressure and temperature: increasing temperature reduces τ , and each particle spends less time oscillating and more time jumping; increasing pressure reverses this and results

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