"Liquid-Gas" Transition in the Supercritical Region: Fundamental Changes in the Particle Dynamics

V. V. Brazhkin,[1] Yu. D. Fomin,[1] A. G. Lyapin,[1] V. N. Ryzhov,[1] E. N. Tsiok,[1] and Kostya Trachenko[2]
[1]*Institute for High Pressure Physics RAS, 142190 Troitsk, Moscow, Russia*
[2]*South East Physics Network and School of Physics, Queen Mary University of London,*
Mile End Road, London E1 4NS, United Kingdom
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Recently, we have proposed a new dynamic line on the phase diagram in the supercritical region, the Frenkel line. Crossing the line corresponds to the radical changes of system properties. Here, we focus on the dynamics of model Lennard-Jones and soft-sphere fluids. We show that the location of the line can be rigorously and quantitatively established on the basis of the velocity autocorrelation function (VAF) and mean-square displacements. VAF is oscillatory below the line at low temperature, and is monotonically decreasing above the line at high temperature. Using this criterion, we show that the crossover of particle dynamics and key liquid properties occur on the same line. We also show that positive sound dispersion disappears in the vicinity of the line in both systems. We further demonstrate that the dynamic line bears no relationship to the existence of the critical point. Finally, we find that the region of existence of liquidlike dynamics narrows with the increase of the exponent of the repulsive part of interatomic potential.

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A liquid near the melting curve has much more in common with a solid than with a gas. For example, a liquid supports transverse collective modes at high frequency that endow the liquid with shear rigidity at that frequency [1–6]. To denote this state of the liquid, the term "rigid liquid" was proposed [7]. In the rigid liquid, particle motion consists of fairly rare jumps and oscillatory motion between the jumps. This is reflected in relaxation time τ, the time between two consecutive particle jumps at one point in space, being larger than the shortest vibration period τ_0 ($\tau_0 = 2\pi/\omega_0$, where ω_0 is the maximal frequency of transverse modes). This description of liquid dynamics has been proposed by Frenkel [8], and was subsequently rediscovered and used in a number of papers (see, e.g., Refs. [9–11]).

Recently, we have shown that the condition $\tau \approx \tau_0$ defines a line, the Frenkel line on the phase diagram that separates the state of the rigid liquid from the "nonrigid" gaslike fluid [7,12–14]. Crossing the Frenkel line on temperature increase results in the disappearance of shear rigidity at all frequencies, specific heat reaching $2k_B$, and, importantly, the qualitative change of temperature dependence of key system properties [7,12,13]. The line is universal: it separates two states at arbitrarily high pressure and temperature, and exists in systems where liquid-gas transition is absent.

A particularly interesting consequence of crossing the Frenkel line from above is the appearance of positive sound dispersion (PSD) [7], the increase of the speed of sound at high frequency [4–6]. Recently, an attempt was made to locate the dynamical line on the basis of molecular dynamics simulations of PSD for supercritical Ar [15].

The condition $\tau \approx \tau_0$ is related to the microscopic dynamics at the Frenkel line, although determining the line using this condition can be done in an approximate way only. When τ and τ_0 become comparable, particle motion may not be uniquely separated into oscillations and jumps. Besides, the separation of quasiharmonic oscillations in a liquid into longitudinal and transverse is not rigorously defined at high temperature. For this reason, an important question remains about how to rigorously define the dramatic crossover at the Frenkel line.

The main aim of this work is to identify the dynamic crossover on the basis of uniquely defined physical characteristics: velocity autocorrelation function $Z(t)$ and mean-square displacement $\langle r^2(t)\rangle$. Among other properties, we discuss positive sound dispersion and its behavior at the Frenkel line.

Velocity autocorrelation function (VAF) $Z(t)$ is defined as

$$Z(t) = \langle v(0)v(t)\rangle. \tag{1}$$

It is well known that $Z(t)$ for the gas is a monotonically decaying function, whereas for solids and liquids near melting it has both oscillatory and decaying components (see Refs. [16,17] and references therein). $Z(t)$ for various liquids was studied in detail. In the early paper [18], it was found that $Z(t)$ for supercritical Lennard-Jones (LJ) fluids may contain both liquidlike and gaslike features, although this fact did not attract subsequent attention. Hiwatari and coauthors have found that depending on the density, $Z(t)$ is qualitatively different in soft-sphere (SSp) fluids [19]. This was followed by the attempt to relate the oscillations of $Z(t)$ and atomic vibrations in SSp fluid [20]. No detailed analysis of $Z(t)$ was performed up to date to distinguish the dynamics between systems in the liquid and gaslike fluid states.

Similarly, the time dependence of the mean-square displacement $\langle r^2(t)\rangle$ is qualitatively different in liquids and solids. Consequently, the behavior of $\langle r^2(t)\rangle$ at long times can be used to calculate the diffusion coefficient in liquids and determine melting and crystallization or vitrification points. At the long time limit, the diffusion coefficient D is related to the mean-square displacement as $D = \langle r^2(t)\rangle/6t$. Evidently, the time dependence of $\langle r^2(t)\rangle$ in liquids and gases should be different at short times, yet no detailed analysis of $\langle r^2(t)\rangle$ was performed in this time regime.

We note that the second time derivative of $\langle r^2(t)\rangle$ is proportional to $Z(t)$. Indeed, using the well-known equation (see, for example, Ref. [16])

$$\langle r^2(t)\rangle = 6\int_0^t (t-s)Z(s)ds,$$

one has

$$\partial^2/\partial t^2\langle r^2(t)\rangle = 6Z(t). \tag{2}$$

Therefore, the analysis of the second derivative of $\langle r^2(t)\rangle$ and $Z(t)$ is formally equivalent.

We have studied LJ liquid and SSp liquids with different exponent n and in a wide range of parameters. The phase diagram of the SSp system corresponds to the equation $\gamma = \rho\sigma^3(\varepsilon/k_BT)^{3/n} = \text{const}$. Here, the values of $\gamma = 2.33$ for $n = 6$; $\gamma = 1.15$ for $n = 12$, and $\gamma = 0.942$ for $n = 36$ have been calculated using the data obtained in Ref. [21]. In the simulations of the LJ liquid, the system size varied depending on the density reaching 4000 particles at the highest density. The equations of state were integrated using the velocity Verlet algorithm; the systems were simulated in the number of particles-volume-energy ensemble. The usual equilibration and production runs consisted of 1.5×10^6 steps, with the time step of 0.001 in LJ units. The SSp system consisted of 1000 particles, with the time step of 0.0005 in reduced units. The following critical parameters, averaged from literature sources, were used for the LJ system: $\rho_c = 0.314$, $T_c = 1.31$, and $P_c = 0.13$. The temperature corresponding to $c_V = 2.0$ was determined from the dependence of the isochoric heat capacity on temperature along the isochors. The dispersion of the longitudinal collective excitations $\omega_L(q)$ has been calculated for both LJ and SSp systems using the same approach as in Ref. [15]. The dispersion has been analyzed at different temperatures along several isochors.

We analyze the temperature dependence of $Z(t)$ and $\langle r^2(t)\rangle$ along several isochors and isobars. We show $Z(t)$, $\langle r^2(t)\rangle$ and its second derivatives at several temperatures for both LJ and SSp systems in Fig. 1, and observe that they qualitatively change with temperature. $Z(t)$ is oscillatory at low temperature, but decreases monotonically at high. We propose that this qualitative change can be used as a mathematically rigorous criterion to define the Frenkel line.

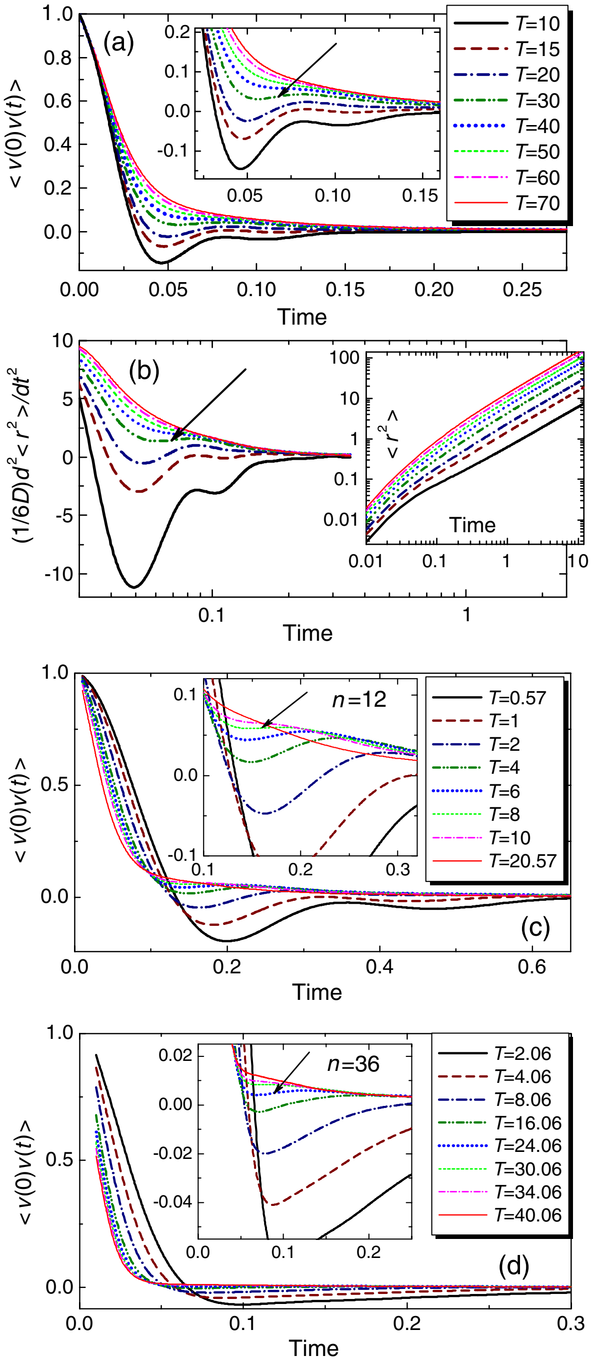

FIG. 1 (color online). Time dependences of VAF $Z(t)$ for the LJ liquid ($P = 200$, pressure is in the LJ units) (a) SSp systems with $n = 12$ (c) and $n = 36$ (d) ($\rho = 1$, density is in the standard soft-sphere units), and the second derivative of the mean-square displacement (b) for the LJ liquid ($P = 200$, pressure is in the LJ units). Insets in (a),(c), and (d) show detailed pictures; inset in panel (b) shows time dependences of mean-square displacement. The vertical arrows correspond to the disappearance of oscillations.

More specifically, the presence of both decreasing and increasing parts of $Z(t)$ implies that the projection of velocity on the direction of motion changes its sign on average, i.e., it signifies the presence of an oscillatory component of motion. Consequently, the temperature at the Frenkel line can be naturally chosen at the "critical" temperature at which minima and maxima of the function in question disappear. We observe that the second derivatives of $\langle r^2(t)\rangle$ have the same functional time dependence as $Z(t)$, consistent with Eq. (2). The coincidence of $\partial^2/\partial t^2\langle r^2(t)\rangle$ and $Z(t)$ and their temperature evolution serves as a self-consistency check in our calculations.

The line corresponding to the change of dynamics according to the above criterion is shown in Fig. 2. In Fig. 2(a) we observe that the temperature of the calculated line is about 1.5–1.7 times lower than the line approximately defined from one of the previous criterion, $\tau \approx \tau_0$. The difference is related to the uncertainty in determining high-frequency longitudinal and transverse oscillations on the basis of visual analysis of trajectories made in Refs. [7,12,13]. We also note that for the LJ system at high pressure, the temperature of the Frenkel line exceeds the melting temperature by a factor of 4–5 on the isobar.

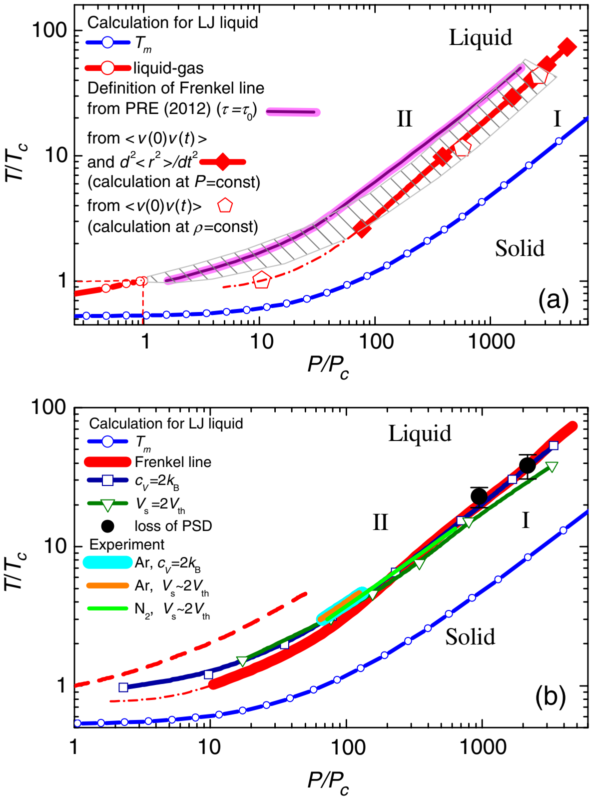

FIG. 2 (color online). (P, T) phase diagram of the LJ liquid in the relative critical coordinates. Panel (a) compares previous criteria of the Frenkel line from Ref. [7]. The shaded region covers all experimental and calculated curves from Ref. [7], together with the Frenkel line calculated in this work. Panel (b) compares positions of the Frenkel line found in this work with calculated and experimental curves and points defined by different criteria (see Ref. [7] and references therein). Black circles correspond to the disappearance of PSD under heating calculated in the present work. Red dashed line in panel (b) shows the dynamic line proposed in Ref. [15]. In all cases I corresponds to the rigid liquid state and II to the nonrigid gaslike state.

Importantly, we observe in Fig. 2(b) that the calculated line perfectly agrees with all other experimental and theoretical criteria of the Frenkel line proposed previously [7]. We therefore find that the phase diagram of the LJ system contains a sharp boundary separating the states of the rigid liquid and nonrigid gaslike state.

For both LJ and SSp systems, we study the dispersion of the longitudinal collective mode $\omega_L(q)$. We detect PSD in both LJ and SSp systems at low temperature, and find that PSD disappears on temperature increase quite close to the calculated Frenkel line. The existence of PSD in the SSp system at low temperatures (Fig. 3) is an important result. It means that the presence or absence of PSD is not related to the continuation of the boiling curve and the critical point whatsoever, contrary to the previous discussions [6,15]. Rather, PSD and its crossover are purely dynamic in origin.

In Figs. 4 we show the calculated Frenkel line on the phase diagrams for the SSp system with $n = 6$, 12, and 36. We note that the terms gas and liquid are not appropriate for the SSp system with no vapor-liquid coexistence curve; nevertheless, the qualitative change of the particle dynamics from the liquidlike to gaslike takes place in this system

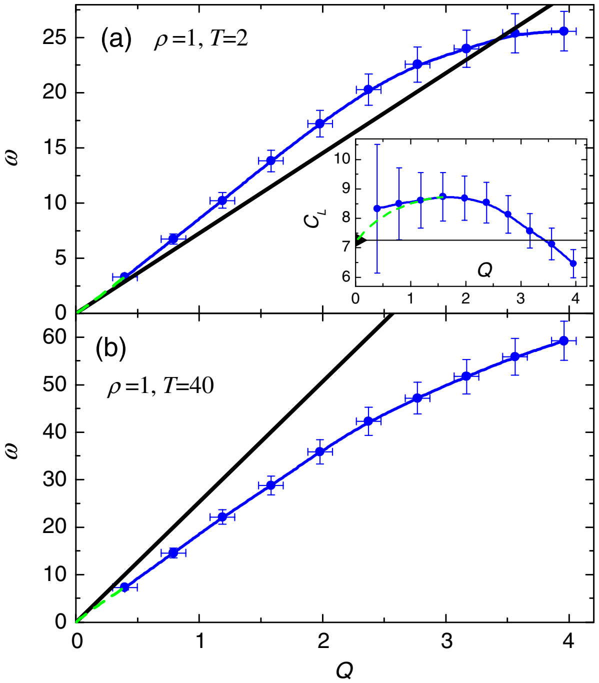

FIG. 3 (color online). Dispersion curves $\omega(Q)$ (blue circles with bars) for the simulated soft-sphere systems with $n = 12$ at low (a) and high (b) temperatures. The inset shows the longitudinal velocity $C_L = \omega/Q$ vs wave vector Q dependence for the case (a), illustrating the PSD. Thick solid lines in panels (a) and (b) and the triangle in the inset correspond to the adiabatic sound velocity at $Q = 0$.

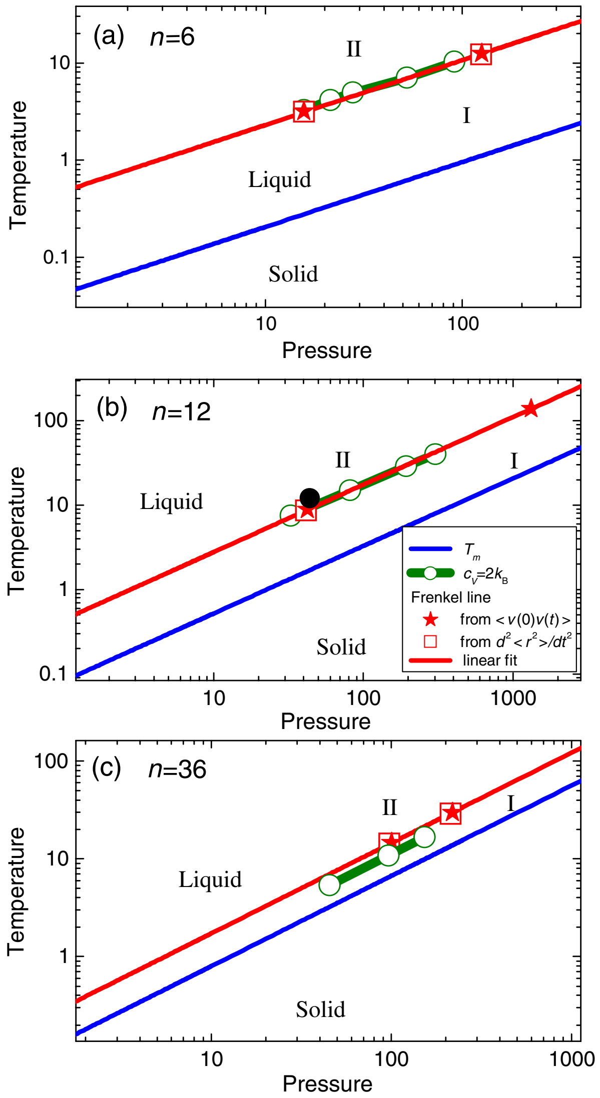

FIG. 4 (color online). (P, T) phase diagrams of the simulated soft-sphere systems with $n = 6$ (a), $n = 12$ (b), and $n = 36$ (c), comparing the location of the Frenkel lines with the lines calculated from the criteria $c_V = 2k_B$. The black circle corresponds to the calculated in present work disappearance of PSD under heating. In all cases I corresponds to the rigid liquid state and II to the nonrigid gaslike state.

too. Importantly, we observe that the dynamic crossover line calculated on the basis of $Z(t)$ perfectly coincides with the line that corresponds to $c_v = 2k_B$, one of the main criteria of the Frenkel line [7]. Indeed, as discussed earlier [7,22,23], liquid specific heat reduces from $3k_B$ to $2k_B$ when $\tau \approx \tau_0$, corresponding to the potential energy of shear modes becoming zero due to the loss of shear modes at all frequencies. The perfect coincidence of the crossover lines calculated on the basis of $Z(t)$ and $c_v = 2k_B$ serves as an important self-consistency check of our theory of the dynamic crossover at the Frenkel line. We also note that the calculated line corresponds to the appearance of PSD at low temperature [see Fig. 4(b)].

Interestingly, the increase of the exponent n results in the narrowing of the P, T region where the quasiharmonic rigid liquid exists. For the SSp system, the ratio of the temperature at the Frenkel line to that at the melting line on the isobar is 11.2 for $n = 6$; 5.3 for $n = 12$, and 2.2 for $n = 36$ (see Fig. 4). This behavior is consistent with our earlier findings [7,12] that for $n \approx 50$–60, the line corresponding to $c_v = 2k_B$ moves under the melting line; i.e., the region of existence of quasiharmonic rigid liquid above the melting line disappears. It should be mentioned that for large values of exponents governing the repulsion n the criterion of the dynamic crossover based on $Z(t)$ no longer applies. The oscillation amplitude becomes extremely small for $n > 50$, and the oscillations become irregular themselves. Physically, this means that particles of the fluid spend most of their time outside the field of action of the potential, and move ballistically as in a gas. This is also the reason for a slight discrepancy of the Frenkel line calculated from $Z(t)$ and $c_v = 2k_B$ for $n = 36$ [see Figs. 4(c)].

As discussed earlier [7,12–14], the Frenkel line and related physics bear no relationship to various versions of a “thermodynamic” continuation of the boiling line, the Widom line. This is particularly apparent in our finding that the dynamic crossover at the Frenkel line, including the crossover of PSD, exists in the SSp system where the liquid-gas transition and the critical point are absent altogether. Furthermore, as is seen in Fig. 2(b), the Frenkel line for the LJ system lies in the range of temperatures that are lower than the critical temperature, and starts from the boiling region at temperature $T \approx 0.7$–$0.8T_c$. In relation to this, we note that at temperature higher than 0.75–$0.85T_c$, a fluid, as a rule, does not possess a cohesive state (the dependence of the free energy on volume has no minimum), implying that the upper region of the boiling curve should be rather considered as the gas-gas transition (see, e.g., Ref. [24]).

As mentioned above, there has been a recent attempt [15] to determine the dynamic line for supercritical Ar on the basis of molecular dynamics simulations of the PSD [it is shown in Fig. 2(b) as a dashed line]. The line proposed in Ref. [15] is notably different from the Frenkel line calculated in our work. The PSD is not a fundamental phenomenon on its own: as was discussed a long time ago [8], the existence of PSD is simply the result of the presence of high-frequency transverselike collective excitations. These excitations disappear at the Frenkel line. The disappearance of PSD is therefore only one of many consequences of the dynamic crossover at the Frenkel line rather than its origin. The PSD in the SSp system additionally points to the inconsistency of using the combination of thermodynamic continuation of the boiling line. Moreover, quantifying PSD in molecular dynamics simulations suffers from large uncertainty, and cannot be, in our view, used as a convenient criterion to establish the location of the dynamic line. It suffices to note that calculated parameters at which PSD disappears for Ar, calculated by the same authors [6,15], differ widely. Indeed, at $T = 3.8T_c$, PSD disappears at $P < 80P_c$ according to Ref. [6], and at $P < 30P_c$ according to Ref. [15].

In summary, we proposed a criterion to locate the dynamic Frenkel line on the phase diagram of fluids that is both mathematically rigorous and convenient for simulations. The calculated Frenkel line for the LJ and SSp systems coincides with various experimental data for rare-gas fluids as well as with the data calculated on the basis of other important physical criteria such as $c_v = 2k_B$. For the LJ system, the Frenkel line starts from the boiling curve at $T \approx 0.7$–$0.8T_c$. The region of the rigid liquid shrinks with the increase of the exponent of the repulsive part of interparticle potential. The new criterion opens an exciting possibility to calculate and map the dynamical line for various liquids with different types of structure and interactions.

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