

# Universal crossover of liquid dynamics in supercritical region

V. V. Brazhkin<sup>1)</sup>, Yu. D. Fomin, A. G. Lyapin, V. N. Ryzhov, K. Trachenko<sup>×</sup>

*Institute for High Pressure Physics, 142190 Troitsk, Russia*

<sup>×</sup>*South East Physics Network and School of Physics, Queen Mary University of London, E1 4NS London, UK*

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We demonstrate that all liquids in supercritical region may exist in two qualitatively different states: solid-like and gas-like. Solid-like to gas-like crossover corresponds to the condition  $\tau \approx \tau_0$ , where  $\tau$  is liquid relaxation time and  $\tau_0$  is the minimal period of transverse waves. This condition corresponds to the loss of shear stiffness of a liquid at all frequencies and defines a new narrow crossover zone on the phase diagram. We show that the intersection of this zone corresponds to the disappearance of high-frequency sound, qualitative changes of diffusion and viscous flow, increase of particle thermal speed to half of the speed of sound and reduction of the constant volume specific heat to  $2k_B$  per particle. The new crossover is universal: it separates two liquid states at arbitrarily high pressure and temperature, and even exists in systems where liquid – gas transition and the critical point are absent overall.

A typical  $T-P$ -diagram implies that a liquid is separated from a gas by the boiling line ending at the critical point and only one single state exists for all pressures and temperatures above the critical point. In present paper we propose that an important qualitative change in a liquid behavior takes place even in supercritical state on crossing narrow crossover zone. We begin our discussion with the introduction of the liquid relaxation time  $\tau$ :  $\tau$  is the average time between two consecutive atomic jumps in a liquid at one point in space [1]. The motion of an atom in a liquid consists of two types: vibrational motion around an equilibrium position as in a solid and diffusive motion between two neighboring positions as in a gas, where typical diffusion distances exceed vibrational distances by about a factor of ten (Fig. 1a–c). Therefore, atomic motion in a liquid combines both elements of the short-amplitude vibrational motion as in a solid and the large-amplitude ballistic-collisional motion as in a gas. This approach was successfully used for last years to calculate the thermodynamic and dynamic properties of liquids near melting temperatures [2, 3]. In the paper we show that the point at which the solid-like motion disappears, leaving only the gas-like motion, marks the change of most important properties of a liquid.

The value of  $\tau$  decreases with temperature increase, spanning many orders of magnitude. On the other hand, the minimal (Debye) vibration period,  $\tau_0$  ( $\tau_0 \approx (0.1-1)$  ps), is weakly temperature-dependent especially at isochors, and is mostly defined by interactions in a given system. At certain high temperature the solid-

like vibration character ceases (Fig. 1a, d, e). This point is reached when  $\tau$  becomes comparable to  $\tau_0$ :

$$\tau \approx \tau_0. \quad (1)$$

In the following discussion, we consider  $\tau$  as the average time it takes an atom to move the average interparticle distance  $a$ . Then,  $\tau$  quantifies the motion envisaged by Frenkel [1], where an atom jumps distance  $a$  during time  $\tau$  between two equilibrium positions at low temperature as well as the motion at high temperature where two equilibrium positions are absent altogether and the motion between collisions is ballistic as in a gas. Here,  $\tau$  is the time between collisions. We note that for  $\tau > \tau_0$  where dynamics is mostly vibrational, the atomic jumps take place by activation over the barrier created by the potential energy of interaction [1]. Therefore, the transition from solid-like vibrations to continuous gas-like ballistic motion takes place when kinetic energy of a particle becomes comparable to potential energy of their interaction. Hence, condition (1) implies crudely

$$3k_B T/2 \sim E_{\text{pot}}. \quad (2)$$

The condition (1) and other conditions considered below correspond to approximate equality. Nevertheless in a liquid there are definite  $T-P$ -conditions corresponding to the loss of transverse-like vibrations in the excitation spectra, hence we can speak about more or less definite line instead of wide crossover. Below we show that it leads to important qualitative changes of the system behavior.

If observation time is smaller than  $\tau$ , the local structure of a liquid does not change, and is the same as that of a solid. This enabled Frenkel to predict that a liquid

<sup>1)</sup>e-mail: brazhkin@hppi.troitsk.ru

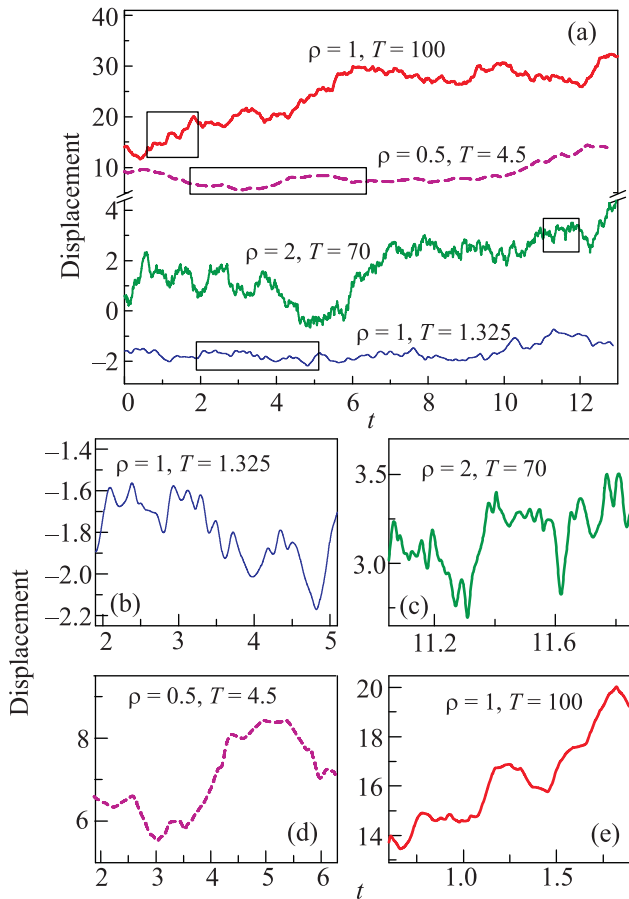


Fig. 1. (Color online) Examples of particle trajectories ( $x$ -coordinate) for the Lennard–Jones (LJ) liquid at different conditions, presented in LJ-units ( $\rho_c = 0.314$ ,  $T_c = 1.31$ ). Panels (b)–(e) show selected fragments from (a). Cases (b) and (c) correspond to the rigid state where vibrations are present; (d) and (e) correspond to collisional motion in the non-rigid state; both time and displacement are in standard

should maintain solid-like shear waves at all frequencies  $\omega > 2\pi/\tau$  [1]. This prediction was later confirmed experimentally for different kinds of liquids [4–6]. The maximum oscillation frequency available in the system is  $\omega_0 = 2\pi/\tau_0$ . Therefore, solid-like shear waves exist in the range  $2\pi/\tau < \omega < 2\pi/\tau_0$ . Consequently, condition (1) ( $\tau \approx \tau_0$ ) corresponds to the complete loss of shear waves. The ability of liquids to flow is associated with zero shear resistance at small frequencies. On the other hand, condition (1) marks the qualitative change, from the physical point of view, of system elastic properties: shear resistance is lost completely, at all frequencies available in the liquid. Therefore, condition (1) marks the crossover between a solid-like “rigid” liquid, where rigidity exists in a certain frequency range and a gas-like “non-rigid” liquid which can not sustain rigidity at any frequency.

The qualitative change in atomic dynamics, defined by Eq. (1), has important consequences. Lets approach the liquid from low temperature where  $\tau > \tau_0$ . The speed of sound in a liquid or a solid,  $V_s$ , is defined from the dispersion relation,  $\omega = V_s k$ . Using linear Debye approximation and taking maximum frequency  $\omega$  as Debye frequency  $\omega_0 = 2\pi/\tau_0$ , and  $k_{\max} = \pi/a$  gives  $V_s = 2a/\tau_0$ . Lets now approach the liquid from high temperature where oscillatory motion is lost, and recall that  $\tau$  is the time between two consecutive collisions over distance  $a$ . Then,  $V_{th} = a/\tau$ , where  $V_{th}$  is particle thermal velocity. Therefore, condition (1) implies

$$V_s \approx 2V_{th}. \quad (3)$$

The physical meaning of condition (3) is that particles cease to feel elastic resistance of the medium. We note that Eq. (3) is based on the same physical grounds as in Eq. (2). Indeed, the speed of sound is governed by the elastic moduli, which are in turn proportional to the potential energy of the system per unit volume. However the proportionality coefficient in (2) may significantly (several times) differs from 1.

Another important consequence of Eq. (1) is related to the phenomenon of “high frequency sound”, which is the increase of the speed of sound at high frequencies. Frenkel predicted [1] that this effect should exist for frequencies  $\omega > 2\pi/\tau$ . The viscoelastic model was later developed, including memory function formalism, non-local mode coupling theory etc. [7–11]. The “high frequency sound” was observed in numerous experiments, receiving particular attention since the development of inelastic  $X$ -ray techniques [12–15]. The condition (1) indeed matches to the region at which the positive dispersion disappears completely, because, as discussed above, this crossover corresponds to the complete loss of shear waves that can exist in a liquid.

The change of the character of atomic diffusion in the liquid at the crossover (1) occurs at a particular value of diffusion constant  $D^*$ . When  $\tau \approx \tau_0$  at the crossover (1), we have

$$D^* \approx a^2/6\tau_0.$$

It was found that liquids loose their elastic properties in the vicinity of the critical point [16, 17]. Both  $a^2$  and  $\tau_0$  decrease with pressure only slightly and for crude estimation of the crossover (1) at moderate pressures, we can use the condition

$$D = D^* \approx D_c \quad (4)$$

(where  $D_c$  is the diffusion constant at the critical point).

Importantly, condition (1) corresponds to the crossover between two different qualitative temperature dependencies of diffusion  $D$  and viscosity  $\eta$ .

At low temperature,  $\tau \sim \exp(U/T)$ , where  $U$  is the activation barrier. Then,  $D \sim a^2/\tau \sim \exp(-U/T)$ . On the other hand, when  $\tau < \tau_0$  at high temperature,  $\tau$  quantifies thermal motion as discussed above:  $\tau \sim 1/V_{th} \sim 1/T^{1/2}$ , giving  $D \sim T^{1/2}$  for a low density gas or  $D \sim T^\alpha$ , where  $\alpha$  is almost constant for a dense fluid. Therefore, condition (1) gives the crossover of  $D$  from exponential to power-law temperature dependence.

When  $\tau > \tau_0$ ,  $\eta$  almost exponentially decreases with temperature, which can be seen most easily by applying the Maxwell relation  $\eta = G_\infty \tau$ , where  $G_\infty$  is the instantaneous shear modulus. On the other hand, when  $\tau < \tau_0$ ,  $\eta \sim T^{1/2}$ . This follows from applying either the Stokes–Einstein–Debye relationship,  $\eta \sim T/D$  or the Maxwell relationship  $\eta = G_\infty \tau$ , where  $\tau \sim 1/T^{1/2}$  from above and recalling that  $G_\infty$  is proportional to kinetic  $\sim T$  term in this regime [18]. Thus the condition (1) corresponds to the qualitative change in the temperature behavior of viscosity from the exponential decrease at  $\tau > \tau_0$  to the power increase at  $\tau < \tau_0$  and viscosity minimum corresponds to a crossover from potentially dominated to kinetically dominated regime.

It is known that constant-volume specific heat of liquids in supercritical region decreases from about  $3k_B$  per particle around the melting temperature to about  $3k_B/2$  at very high temperatures in supercritical region [19]. The initial decrease was quantitatively on the basis of decreasing contribution of shear modes to liquid energy with temperature [20]. In this model, the liquid thermal energy per atom is

$$E/N = k_B T [3 - (\tau_0/\tau)^3].$$

When  $\tau$  considerably exceeds  $\tau_0$  at low temperature, liquid energy is close to  $3k_B T$  per atom, giving the Dulong–Petit value of specific heat of  $3k_B$ . When  $\tau$  approaches  $\tau_0$  at high temperature shear waves are completely lost at all frequencies, and longitudinal modes only contribute to the heat capacity. The thermal energy becomes  $2k_B T$  per atom, giving the specific heat of  $2k_B$ . Therefore, the condition (1) approximately corresponds to the decrease of the specific heat from its solid-state value to the value of  $2k_B$ :

$$C_V \approx 2k_B. \quad (5)$$

Further decrease of heat capacity corresponds to the loss of longitudinal modes as the temperature is increased until the gas-like state is reached with  $c_V = 3k_B/2$ .

Having discussed the main physical properties that change at the crossover (1), we now provide numerical and experimental evidence supporting our proposal.

We have studied Lennard–Jones (LJ) liquid and Soft Spheres (SSp) liquid with  $n = 12$  in a wide range of parameters, from temperature  $T = 0.6$  (well below the critical point) to  $T = 100.0$  and densities from 0.1 to 2.7 for LJ-liquid,  $T = (0.1–100)$  and density in the range 0.1–3.33 for SSp-liquid with  $n = 12$ . The number of particles in the system, depending on the density was varied up to 4000 and 1000 for the LJ- and SSp-system, respectively. The equilibration and production was simulated for 1.5 million steps and 0.5 million steps for LJ-system and 3.5 million and 0.5 million steps for SSp-system, respectively. The time step was 0.001 LJ-units for LJ-system and 0.0005 for SSp-system.

To calculate the Debye period  $\tau_0$ , we analyzed particle trajectories. At low temperature,  $\tau_0$  was obtained as the average time of oscillatory motion. The value of  $\tau$  was calculated as time it takes a particle to move the distance close to the average inter-particle separation. The values of  $\tau_0$  and  $\tau$  as well as the temperature of disappearance of solid-like vibration motion under heating were also obtained from the analysis of self-intermediate scattering function [8] at different temperatures. All other quantities discussed in the paper were calculated in standard way [21]. Thermodynamic and dynamic data for real fluids (Ar, Ne, and N<sub>2</sub>) were taken from [19].

We have drawn the lines determined by Conditions (1)–(5), for real substances (Ar, Ne, and N<sub>2</sub>) and model particle systems with Lennard–Jones and soft-sphere potentials (Figs. 2 and 3). We have calculated points on the phase diagram that correspond to strict equalities  $\tau = \tau_0$ ,  $3k_B T/2 = E_{pot}$ ,  $V_s = 2V_{th}$ ,  $D = D_c$ , and  $c_V = 2k_B$ .

According to Fig. 2, the position of the crossover line (Condition (1)) for Lennard–Jones system agrees with the line determined by Condition (4) at moderate pressures  $P < (10–10^2)P_c$  and with the lines determined by Conditions (3) and (5) at high pressures  $P > 10P_c$ . At low pressures, the lines determined by Conditions (3) and (5) shift from the crossover line (1) due to critical point anomalies and loss of Debye approximation at low densities. The Condition (2) is not directly based on the Condition (1) and proportionality coefficient in (2) differs from 1 significantly. For a soft-sphere system, the lines determined by the Conditions (1)–(3), and (5) match well over the entire pressure range (Fig. 3), as no critical point and associated anomalies exist for this system. For the soft-sphere system, we also calculate the line of viscosity minimum on isochors which practically coincides with the lines defined by other criteria.

Despite the approximate way in which conditions (2)–(5) correspond to condition (1), all the lines defined

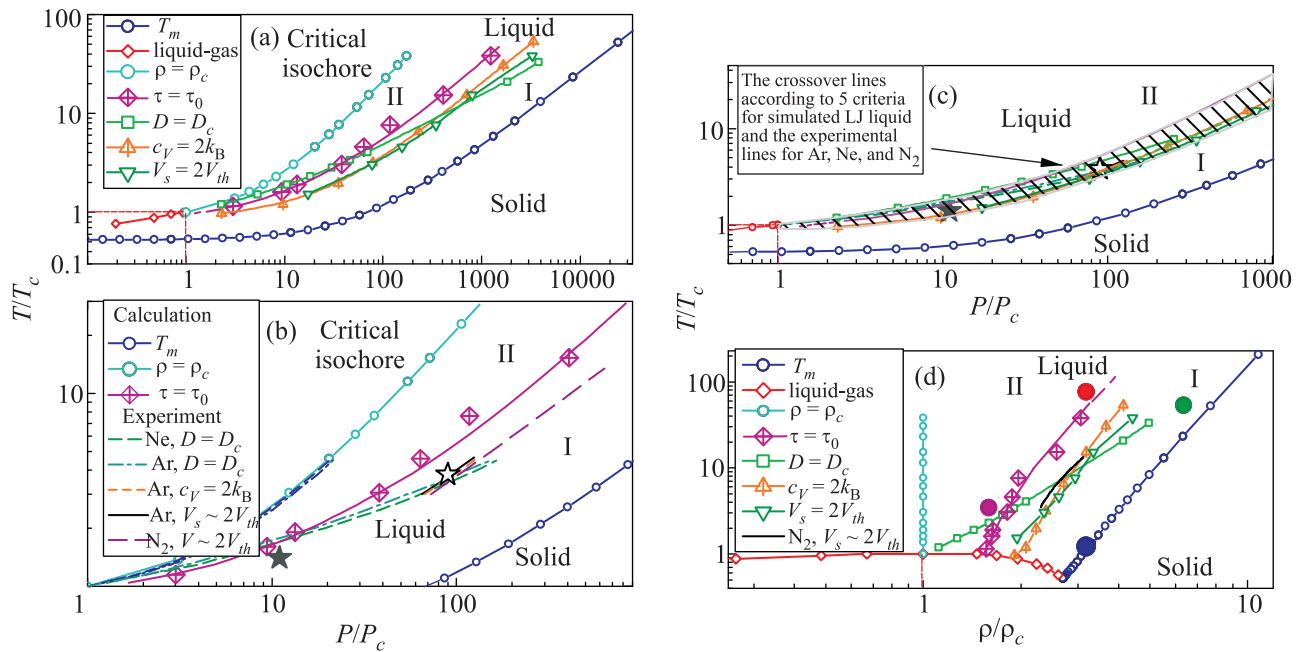


Fig. 2. (Color online)  $T$ – $P$  phase diagram ((a), (b), and (c)) and  $T$ – $\rho$  phase diagram (d) of the LJ-liquid in the relative critical coordinates. Panels (a) and (d) present calculated lines defined by different criteria (see the text). Panel (b) presents some experimental data from [19]. Stars in the panel (b) correspond to known experimental points where liquid loses shear waves and positive dispersion (open symbol for Ar [13] and solid symbol for N<sub>2</sub> [15]). Experimental critical isochors are also shown in panel (b) (dashed for Ne and dashed-dotted for Ar). Experimental data for criterion (3) for nitrogen and points (solid circles) from the simulation of the LJ-system in Fig. 2 (with the same color) are shown in panel (d). Panel (c) illustrates narrow crossover zone according to different criteria both for LJ-system and real liquids. In all cases number I correspond to rigid liquid and II – to non-rigid one. In panel (d) the density from the liquid side is shown for the melting curve

by conditions (2)–(5) are located within quite a narrow range. We note that these lines are located at temperatures that are significantly above the melting line implying that the new dynamic line separates two distinct liquid states and significantly below the isochore, in contrast to the Widom line discussed below in more detail. Importantly, the lines of all conditions (except condition (4) which is approximate and valid only at moderate pressure) lie close to each other in the whole range of pressures and temperatures. Notably, pressure in this range varies by almost four orders of magnitude. We further observe that by only slight variation of the proportionality coefficients in criteria (1)–(3), namely by a factor of 1.3–1.4, the lines defined by these conditions practically coincide, which testifies to the commonality of physical mechanisms underlying the above criteria. The same is true for the criterium (5): The line defined by the condition  $c_V = 1.9k_B$  (note that 1.9 differs from 2 by 5%) coincides with the main line defined by criterium (1).

In addition to model systems, we find good agreement between the theoretical predictions and experimental data for liquid Ar, Ne, and N<sub>2</sub> (Fig. 2). In particular,

we observe a good match between the region of the disappearance of the positive dispersion of sound velocity in liquid Ar [13] and N<sub>2</sub> [15] and the dynamic line (Fig. 2). The qualitative change of the temperature dependencies of viscosity of liquid nitrogen near crossover region is demonstrated at Fig. 4.

Interestingly, crossover lines correspond to density increase with increasing temperature: the relation  $\rho \sim T^k$  is met, where  $k \approx 0.25$  for liquid N<sub>2</sub>, LJ- and SSp-systems (Figs. 2 and 3). Note that for any system of particles with uniform potential, there are scaling relations for physical values [22]. In particular,  $\rho^{n/3}/T = \text{const}$  along the melting line for the SSp-system, giving  $\rho \sim T_m^{1/4}$  for the melting temperature  $T_m$  for  $n = 12$ . The similarity of the dependence of  $\rho(T)$  for the melting and dynamic lines implies similar scaling relations for the dynamic line. This point will be discussed in details elsewhere. As a result, the region of the solid-like “rigid” liquid does not, under any pressures, disappear (Figs. 2 and 3) and the narrow crossover zone continues for arbitrarily high pressures and temperatures.

We note that the line related to condition (2) was considered earlier, at least at low pressures [23, 24]. This

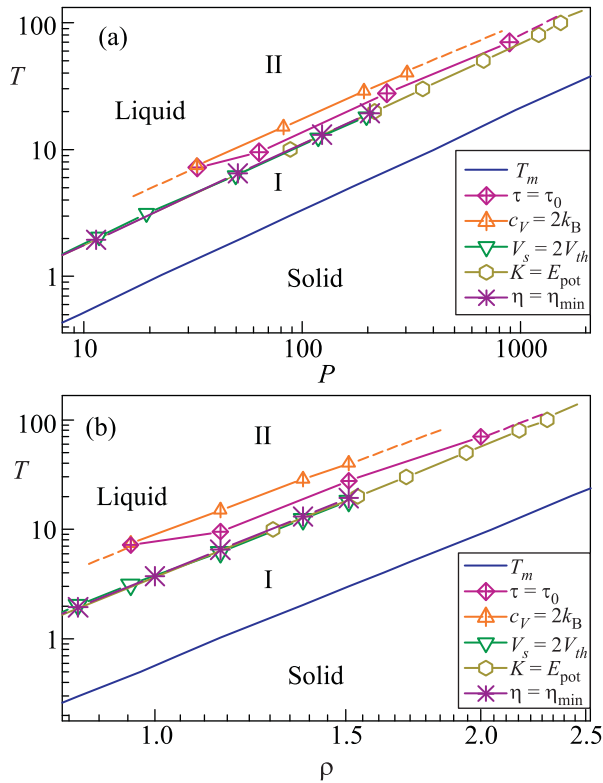


Fig. 3. (Color online)  $T$ - $P$  and  $T$ - $\rho$  phase diagrams of the simulated soft-sphere systems for  $n = 12$  [(a) and (b)]. This figure presents calculated lines defined by different criteria including that for the minimum of viscosity  $\eta$  on isochors. In panel (b) the density from the liquid side is shown for the melting curve; both temperature and pressure are in standard reduced soft-sphere system units

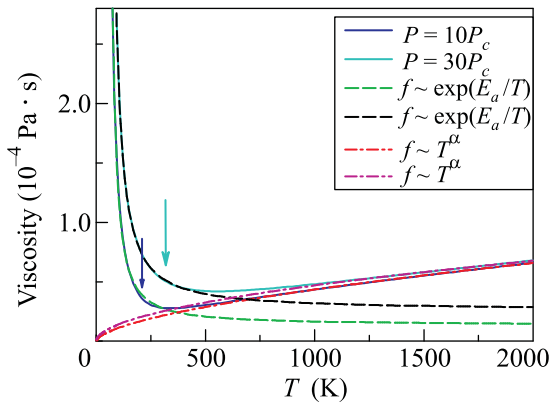


Fig. 4. (Color online) Experimental [19] isobaric temperature dependences of viscosity of nitrogen with asymptotes at low (exponent of inverse temperature) and high (power law) temperatures. Arrow indicates the corresponding temperature of condition (1),  $\tau = \tau_0$ ;  $\alpha = 0.59$  at  $P = 10P_c$  and  $0.53$  at  $P = 30P_c$

line corresponds to percolation of “physical clusters”. A cluster, by definition, is made of particles linked pair-

wise, where a pair of particles is linked if the sum of their relative kinetic and interaction energy is less than zero.

It is interesting to note the recent attempts [13, 14] to link the change in the excitation spectrum to the “thermodynamic” continuation of the boiling curve, the so-called Widom line, the line of the maxima of thermodynamic properties in the vicinity of critical point [25]. From a physical point of view, this extrapolated line is qualitatively different from the dynamic crossover line proposed here. Indeed, the proposed dynamic line is not related to the extrapolation of the boiling curve, and exists in systems where liquid-gas transition and the correspondent Widom line are absent altogether, including SSp-systems and real soft-matter systems (see [26]). In addition, there are several other important differences. We recently have calculated compressibility  $\beta_T$ , expansion coefficient  $\alpha_P$ , heat capacity  $c_P$  and density fluctuations  $\zeta$  for the LJ-system [27]. The lines of maxima of all calculated properties rapidly decrease in magnitude and become smeared at  $T > (2-2.5)T_c$  and  $P > (10-15)P_c$ , and therefore can not be meaningfully extrapolated to higher pressures and temperatures. This is in contrast to the proposed dynamic line which exists for arbitrarily high pressures and temperatures. Finally, apart from the line of the maxima of the heat capacity lying close to the critical isochore, the lines of thermodynamic anomalies correspond to a decrease in the density with temperature increase, in strong contrast to the dynamic line.

We propose to call the crossover line defined by Eq. (1) “Frenkel line”, to honor the contribution of J. Frenkel to the area of liquid dynamics [1]. On the basis relaxation time notion Frenkel made a number of important predictions regarding flow, relaxation as well as elastic and phonon properties of liquids that subsequently formed the microscopic basis of what is now known as “visco-elastic” picture of liquids [1]. The proposed Frenkel line separates a solid-like liquid where solid-like shear waves exist and diffusion regime is jump-like and activated as in a solid, from a gas-like liquid where no shear modes exist and diffusion is collisional as in a gas. This line can be mapped in future experiments using several conditions for liquid properties that we discussed. For molecular and rare-gas liquids the line is situated at “static pressures” experimental condition, e.g. for Ne the condition (1) at  $P \sim 3 \text{ GPa}$  should take place at  $T \sim (1000-1100) \text{ K}$  (approximately 5–6 times higher than the melting temperature). It is important to stress that basic conditions above, (1)–(3) and (5) are not related to liquid-gas transition and to the existence of critical point from the physical point of view, and

continue to operate in systems where the critical point is absent altogether.

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1. J. Frenkel, *Kinetic Theory of Liquids*, Oxford University Press, N.Y., 1946.
2. D. C. Wallace, *Phys. Rev. E* **56**, 4179 (1997).
3. E. D. Chisolm and D. C. Wallace, *J. Phys.: Condens. Matter* **13**, R739 (2001).
4. M. Grimsditch, R. Bhadra, and L. M. Torell, *Phys. Rev. Lett.* **62**, 2616 (1989).
5. T. Pezeril, C. Klieber, S. Andrieu et al., *Phys. Rev. Lett.* **102**, 107402 (2009).
6. S. Hosokawa, M. Inui, Y. Kajihara et al., *Phys. Rev. Lett.* **102**, 105502 (2009).
7. J. P. Boon and S. Yip, *Molecular Hydrodynamics*, Dover, N.Y., 1980.
8. U. Balucani and M. Zoppi, *Dynamics of the Liquid State*, Clarendon, Oxford, 1994.
9. E. Pontecorvo, M. Krischm, A. Cunsolo et al., *Phys. Rev. E* **71**, 011501 (2005).
10. T. Bryk, I. Mryglod, T. Scopigno et al., *J. Chem. Phys.* **133**, 024502 (2010).
11. W-C. Pilgrim and Chr. Morcel, *J. Phys.: Condens. Matter* **18**, R585 (2006).
12. T. Scopigno, G. Ruocco, and F. Sette, *Rev. Mod. Phys.* **77**, 881 (2005).
13. G. G. Simeoni, T. Bryk, F. Gorelli et al., *Nature Physics* **6**, 503 (2010).
14. F. Gorelli, M. Santoro, T. Scopigno et al., *Phys. Rev. Lett.* **97**, 245702 (2006).
15. F. Bencivenga, A. Cunsolo, M. Krisch et al., *Europhys. Lett.* **75**, 70 (2006).
16. F. Bencivenga, A. Cunsolo, M. Krisch et al., *Phys. Rev. Lett.* **98**, 085501 (2007).
17. F. Bencivenga, A. Cunsolo, M. Krisch et al., *J. Chem. Phys.* **130**, 064501 (2009).
18. R. Zwanzig and R. D. Mountain, *J. Chem. Phys.* **43**, 4464 (1965).
19. NIST Chemistry WebBook, <http://webbook.nist.gov/chemistry/>.
20. K. Trachenko, *Phys. Rev. B* **78**, 104201 (2008).
21. V. V. Brazhkin, Yu. D. Fomin, A. G. Lyapin et al., <http://arxiv.org/abs/1104.3414>.
22. W. G. Hoover, S. G. Gray, and K. W. Johnson, *J. Chem. Phys.* **55**, 1128 (1971).
23. A. Coniglio, U. De Angelis, and A. Forlani, *J. Phys. A* **10**, 1123 (1977).
24. X. Campi, H. Krivine, and N. Sator, *Physica A* **296**, 24 (2001).
25. L. Xu, P. Kumar, S. V. Buldyrev et al., *Proc. Natl. Acad. Sci. USA* **102**, 16558 (2005).
26. G. Malescio, *J. Phys.: Condens. Matter* **19**, 073101 (2007).
27. V. V. Brazhkin, Yu. D. Fomin, A. G. Lyapin et al., *J. Phys. Chem. B* DOI: 10.1039/C1JM10889A (2011).