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Frenkel line and solubility maximum in supercritical fluids

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A new dynamic line, the Frenkel line, has recently been proposed to separate the supercritical state into rigid-liquid and nonrigid gaslike fluid. The location of the Frenkel line on the phase diagram is unknown for real fluids. Here we map the Frenkel line for three important systems: CO_2, H_2O, and CH_4. This provides an important demarcation on the phase diagram of these systems, the demarcation that separates two distinct physical states with liquidlike and gaslike properties. We find that the Frenkel line can have a similar trend as the melting line above the critical pressure. Moreover, we discuss the relationship between unexplained solubility maxima and Frenkel line, and we propose that the Frenkel line corresponds to the optimal conditions for solubility.

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Recently there has been a dramatical increase of using supercritical fluids in extraction and purification applications, including in food, nuclear waste, petrochemical, and pharmaceutical industries [1–4]. Supercritical fluids attract significant attention due to their extremely good dissolving power and "tunable" properties. The solubility of supercritical fluids depends on density and diffusivity. Supercritical fluids combine the best of both worlds: high density of liquids and large diffusion constants of gases. Moreover, both of those properties can be tuned over a wide range pressure and temperature above the critical point, optimizing their dissolving ability.

Carbon dioxide, water, and methane are three most commonly used supercritical fluids. In particular, H_2O and CO_2, are both abundant, nonflammable, and nontoxic. They are also "nonpolar" and "polar" solvent, respectively, so they can dissolve "polar" and "nonpolar" solutes, respectively. The critical temperature (T_c) of CO_2 is at 304 K, which is near the room temperature, and the critical pressure (P_c) is 74 bar, which is also accessible. Additionally, CO_2 can be used with cosolvents to modify it into "polar" solvent.

The solubility of variety of solutes have been measured in supercritical CO_2 near T_c as a function of pressure [1]. Interestingly, the experiment shows intriguing solubility maxima above critical temperature: solubility first substantially increases with pressure, followed by its decrease at higher pressure [5–12]. This effect is not currently understood theoretically. Understanding it would lead to more efficient use of supercritical fluids. More generally, it is often acknowledged that wider deployment of supercritical fluids and optimizing their use would benefit from theoretical guidance [1,2].

Until recently, a supercritical state was believed to be physically homogeneous, which means that moving along any path on a pressure and temperature above the critical point does not involve marked or distinct changes. The Frenkel line has recently been proposed, which separates two dynamically distinct states: the gaslike regime where particles only have diffusive motion and the liquidlike regime where particles combine both solidlike quasiharmonic vibrational motion and gaslike diffusive motion [13–15]. This transition takes place when the liquid relaxation time τ approaches the Debye vibration period τ_D. Liquid relaxation time is defined in the usual way as the average time between two consecutive diffusion events (molecular rearrangements between two quasiequilibrium positions) in the liquid at one point in space [16]. When $\tau \approx \tau_D$, the system loses the ability to support shear modes at all available frequencies, up to Debye frequency, and retains gaslike diffusive dynamics only. The Frenkel line starts from 0.7–0.8 T_c at P_c and extends to arbitrarily high pressure and temperature on the phase diagram [17]. There are many ways to locate the Frenkel line on the phase diagram, yet the velocity autocorrelation function (VAF) provides a convenient and mathematically meaningful criterion: the disappearance of oscillations and minima of the VAF correspond to pressure and temperature of the Frenkel line [17].

In this paper, we map the Frenkel line on the phase diagram using molecular dynamic (MD) simulation by calculating VAF. We study the location of the Frenkel line for CO_2, H_2O, and CH_4 on the phase diagram, particularly addressing the slope of the Frenkel line in relation to the melting line. We subsequently compare the Frenkel line with the solubility maximum from experiment [5–7,9] and discuss why the Frenkel line is related to the solubility maxima.

We use DL_POLY MD simulation package [18] and have simulated 4576 CO_2 molecules, 3375 H_2O molecules, and 3375 CH_4 molecules using a constant-pressure-temperature ensemble. The intermolecular potential for CO_2 is the rigid-body nonpolarizable potential based on a quantum chemistry calculation, with the partial charges derived using the Distributed Multipole Analysis method [19]. The intermolecular potential of H_2O is TIP4P/2005, which can describe the intermolecular force very well [20]. The intermolecular potential of CH_4 is taken from Ref. [21]. This potential also shows good accuracy in the supercritical state. We used a cutoff of 12 Å for potential, and the smoothed particle mesh Ewald for long-range forces. We first equilibrate the system during 10 ps and ensure the equilibration at given (P,T) conditions during the subsequent 40 ps. We collect and analyze the result during the following 50 ps. In the range of our simulations, the difference between MD and experimental density from the NIST database [22] is less than 5%. Our pressure range extends to several GPa and includes the pressure used in industrial applications.

It is well known that VAF is a monotonically decaying function in the gas state, whereas it shows damped oscillation

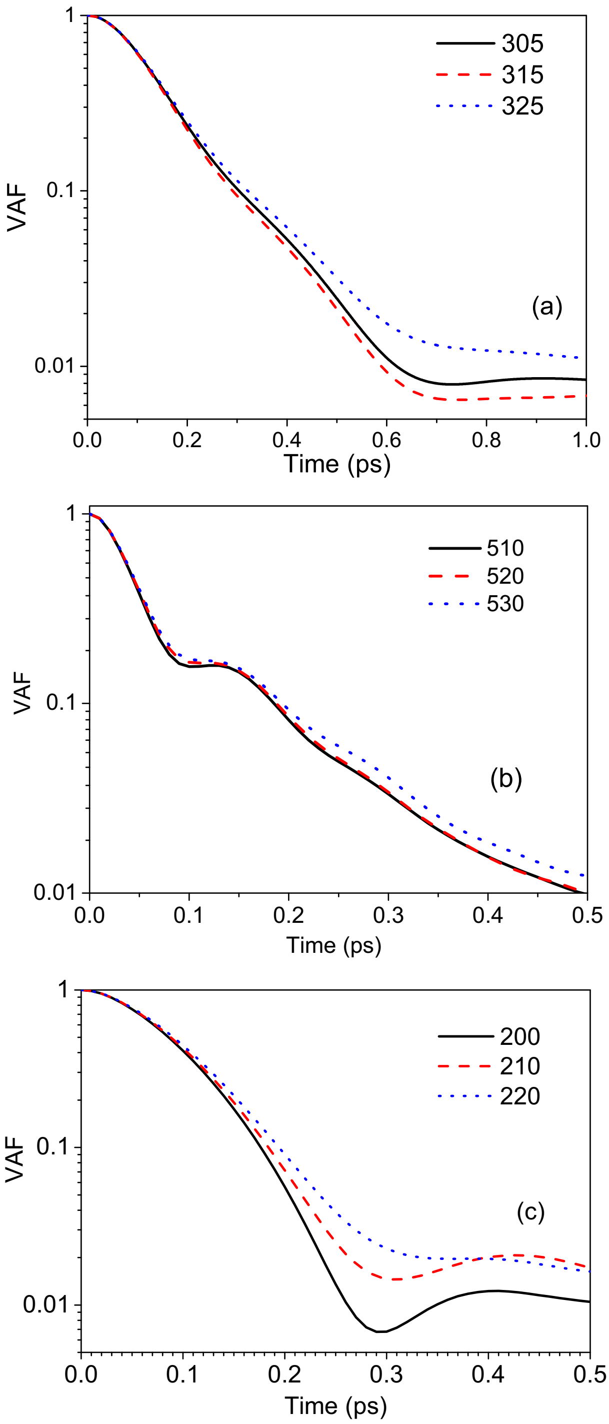

FIG. 1. (Color online) Velocity autocorrelation functions for CO_2 (a), H_2O (b), and CH_4 (c) showing the crossover at the Frenkel line at 900 bar.

in the liquid and solid states. VAF is defined as

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

In previous work [17], it was shown that the minimum of VAF would disappear when the system crosses the Frenkel line in the supercritical state. In Fig. 1 we show representative VAFs for CO_2, H_2O, and CH_4 at 900 bar. We can clearly see that as the temperature increases, the minimum becomes more shallow and finally disappears, which corresponds to the loss of oscillatory component of molecular motion and gives (P,T) for the Frenkel line. We note that the longitudinal mode persists above the Frenkel line, albeit starts disappearing with temperature, starting with the shortest wavelengths [23].

In Fig. 2 we map the Frenkel line for CO_2, H_2O, and CH_4 using the VAF criterion (disappearance of the first minimum). For technologically important CO_2 and H_2O, we show the Frenkel line in both (pressure, temperature) and (density, temperature) coordinates. We also show the melting line [24–27] on the phase diagram.

We observe that the Frenkel line for all three fluids starts from 0.7∼0.8 T_c at P_c, which agrees with our previous result for Lennard-Jones fluids [17]. Notably the Frenkel line does not need to start from the critical point because fundamentally it is related to critical phenomena and exists in systems such as the soft-sphere system where the boiling line and the critical point are absent altogether [17].

We now discuss a relationship between the Frenkel line and the melting line, the relationship that can serve as a useful guide to map the Frenkel line on the phase diagram for any system. As discussed above, the Frenkel line starts slightly below the critical point. At higher pressure, we can predict that the Frenkel line is parallel to the melting line in the log-log plot on the basis of the well-known scaling argument. Indeed, starting from high GPa pressures, the intermolecular interaction is reduced to its repulsive part only, whereas the cohesive attracting part no longer affects interactions (at low pressure, the parallelism between the two lines holds only approximately because the interactions are not well approximated by simple repulsive laws; see below). In a sufficiently wide pressure range, the repulsive part can be well approximated by several empirical interatomic potentials such as the Buckingham-type functions or Lennard-Jones potentials with inverse power-law leading terms at short distances $U \propto \frac{1}{r^n}$. For the inverse power law, a well-known scaling of pressure and temperature exists: the system properties depend only on the combination of TP^γ, where γ is uniquely related to n. Consequently, $TP^\gamma = \mathrm{const}$ on all (P,T) lines where the dynamics of particles changes qualitatively, as it does on both the melting line and the Frenkel line. This implies that the Frenkel and melting lines are parallel to each other in the double-logarithmic plot, the insight that we have recently used to construct the Frenkel line for molecular hydrogen [28].

We have recently simulated the Frenkel line in supercritical iron and, consistent with the above discussion and current results, have found that the Frenkel line is parallel to the melting line in the logarithmic plot [29].

Although our simulations were in the practically useful range of pressure and did not extend to high enough pressure to meet the condition above, we observe that the Frenkel line has a similar trend as the melting line: for CO_2, the slopes of the Frenkel line and the melting line both start to increase around 1000 bar. For H_2O, both lines are flat below 1000 bar, but their slopes start increasing at higher pressure. We also observe a similar slope increase for methane simultaneously around 1200 bar.

The speed of sound is one of the important properties that show qualitative changes in the supercritical state. Notably, the speed of sound decreases with temperature below the Frenkel

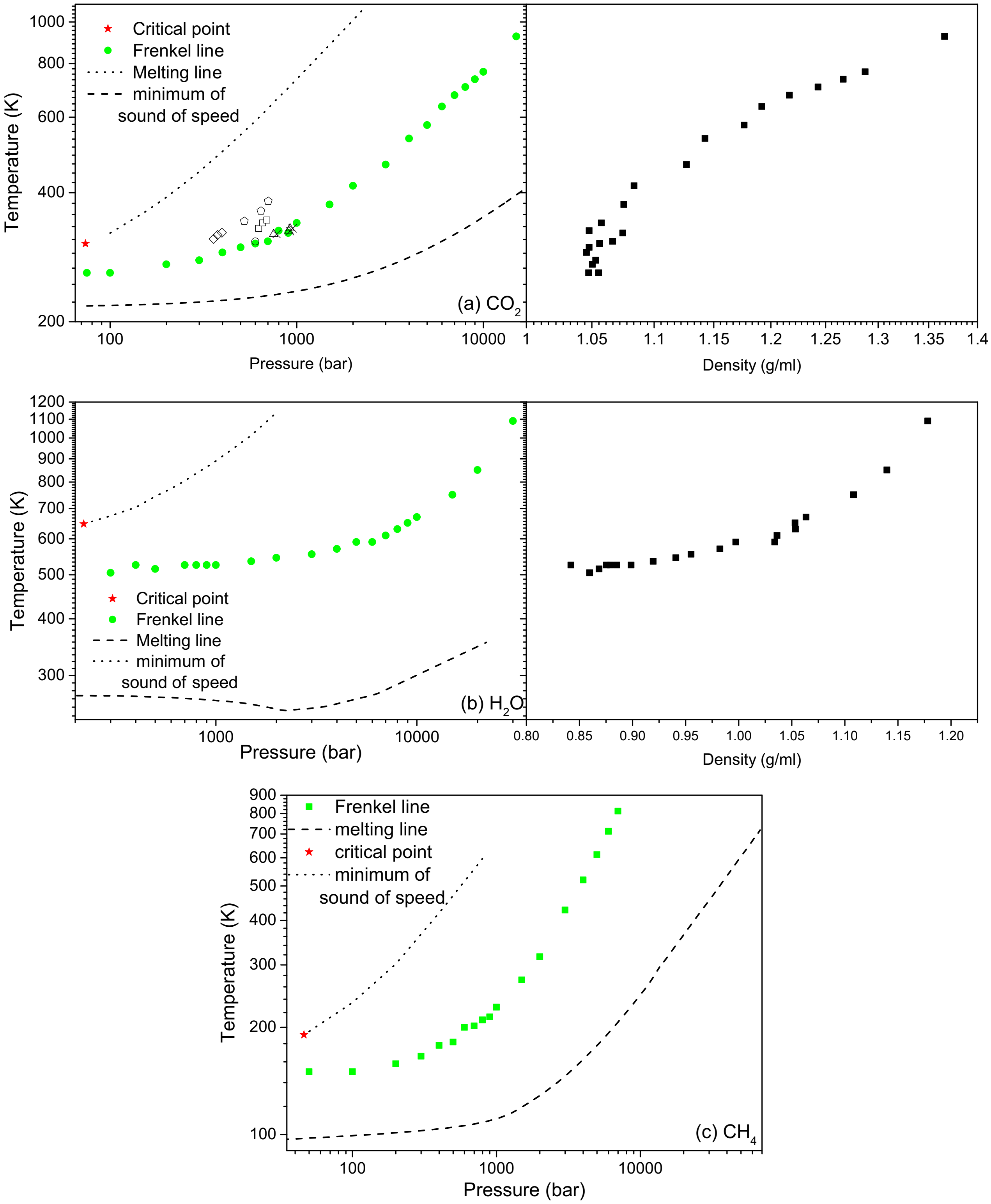

FIG. 2. (Color online) The Frenkel line for CO_2, H_2O on the pressure-temperature (left) and density-temperature (right) phase diagram. The Frenkel line for CH_4 is shown in the pressure-temperature diagram. The solubility maximums of different solutes in supercritical CO_2 are shown in panel (a). The open circles are the solubility of β carotene [9]; the squares are 1,4-bis-(octadecylamino)-9,10-anthraquinone [5]; triangles are 1,4-bis-(n-alkylamino)-9,10-anthraquinone [6]; diamonds are biphenyl [7]; pentagons are adamantane [10]; crosses are 1,4-bis-(hexadecylamino)-9,10-anthraquinone [11].

line, as in liquids and solids, but increases with temperature sufficiently above the line, as in gases [13–15]. We note that the minima of the speed of sound are not absolute in the sense that their positions depend on the path on the diagram (the position of the minimum along isobars, isochors, and isotherms can be different). The scaling argument above implies that if the minima of the speed of sound correspond to the qualitative change of particle dynamics, the line of these minima should be approximately parallel to the Frenkel line. In Fig. 2 we show pressure and temperature that correspond to the minimum of the speed of sound as deduced from the NIST database [22]. We observe that the line of the speed of sound minimum is approximately parallel to the Frenkel line at high pressure as predicted.

To discuss the relationship between the solubility and the dynamic property of supercritical fluid, we show isothermal solubility maxima of different solutes in CO_2 [5–11], on the phase diagram [Fig. 2(a)]. Importantly, we observe the points of solubility maxima are close to the Frenkel line. The solubility of maxima of several solutes, such as β carotene, 1,4-bis-(n-alkylamino)-9,10-anthraquinone, and 1,4-bis-(hexadecylamino)-9,10-anthraquinone coincide with the Frenkel line.

We now explain the proximity of the solubility maxima and Frenkle line, as follows. Let us fix a temperature above the critical point to the left of the Frenkel line and increase the pressure (moving horizontally to the right in Fig. 2). Pressure has two competing effects on diffusion. On one hand, it increases density and hence the contact area and cleaning (dissolving) efficiency. On the other hand, the density increase results in decreasing the diffusion constant. Indeed, at the Frenkel line, where the molecular dynamics acquires the oscillatory component, molecular rearrangements become markedly less frequent, in contrast to the gaslike dynamics above the line where the oscillatory component of motion is absent. Therefore, at the Frenkel line, the supercritical fluid has maximal density possible at which the diffusion is still in the fast gaslike regime and not in the slow liquidlike regime. The optimum combination of these two properties gives solubility maxima.

The data for solubility maximum for H_2O and CH_4 are not available. From Figs. 2(b) and 2(c), we see the reason why it is difficult to perform these in experiments. In the case of water, the pressure of Frenkel line is ~9000 bar at T_c, which is ~40 times of P_c of H_2O (220.64 bar). Although the pressure of CH_4 is not too high (~600 bar) at T_c, the pressure increases to ~4000 bar at room temperature. In both cases, their pressure is much higher than P_c. Compared with them, CO_2 is located ~1000 bar at T_c, which is relatively more affordable in experiment. We propose the Frenkel line serve as a predictive tool to locate the solubility maxima on the phase diagram. This provides a useful guide for future experiments.

We note that the increase of pressure along the Frenkel line results in several other interesting and potentially important effects such as the increase of the fluid density and diffusion constant as well as the appearance of the viscosity minimum [13–15,17]. In addition, surface tension tends to zero around and above the critical point so that that the problem of wetting is avoided. Accordingly, these conditions may favor other important properties of supercritical fluids: for example, the speed of chemical reactions may have a maximum close to the Frenkel line. In this and other cases, supercritical technology will further benefit from theoretical guidance and receive an impetus for using the supercritical fluids in the hitherto unknown range of 1–10 kbar.

In summary, we mapped the Frenkel line for three important systems: CO_2, H_2O, and CH_4. This provides an important demarcation on the phase diagram of these systems, the demarcation that separates two distinct physical states with liquidlike and gaslike properties. We proposed that the Frenkel line can serve as a important guide to estimate the location of solubility maxima, so that the cleaning and dissolving abilities of the supercritical fluids are optimized.

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