PHYSICAL REVIEW E **91**, 022111 (2015)

Thermodynamic properties of supercritical carbon dioxide: Widom and Frenkel lines

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(Received 11 September 2014; published 9 February 2015)

Supercritical fluids are widely used in a number of important technological applications, yet the theoretical progress in the field has been rather moderate. Fairly recently, a new understanding of the liquidlike and gaslike properties of supercritical fluids has come to the fore, particularly with the advent of the Widom and Frenkel lines that aim to demarcate different physical properties on the phase diagram. Here, we report the results of a computational study of supercritical carbon dioxide, one of the most important fluids in the chemical industry. We study the response functions of CO_2 in the supercritical state and calculate the locations of their maxima (Widom lines). We also report the preliminary calculations of the Frenkel line, the line of crossover of microscopic dynamics of particles. Our insights are relevant to physical processes in the atmosphere of Venus and its evolution.

DOI: 10.1103/PhysRevE.91.022111 PACS number(s): 64.60.Kw, 64.60.ah, 64.60.fd

I. INTRODUCTION

It is well known that many thermodynamic functions, including, for example, heat capacity, isothermal compression, and heat expansion coefficients, demonstrate maxima in the vicinity of a critical point. Investigation of supercritical maxima has been important in the theory of phase transitions and critical phenomena as well as in technological applications. In addition to theoretical interest, supercritical fluids are widely used in the chemical industry due to their high solubility, rate of chemical reactions, etc.

Recently, it was proposed that the locations of maxima of different quantities lie not far from each other in the (ρ,T) plane or the (P,T) plane. In this case one introduces a single line of supercritical maxima. This line was named a Widom line [1]. However, later it was shown that, even in the simplest liquids like Van der Waals [2], Lennard-Jones (LJ) [3,4], square well [5], and a simple toy model proposed in Ref. [6], the maxima of different thermodynamic functions can be rather far away from each other. Moreover, the lines of maxima of different quantities were found to behave qualitatively differently: temperature increase gives higher density for some lines but lower density for others. As a result, all curves rapidly diverge and form a wide bunch of lines rather than a single line. The Widom line of water was considered in Refs. [7–9], where a very similar qualitative behavior of supercritical maxima of water and model liquids was found. Yet the locations of the maxima points in (ρ,T) or (P,T) planes are reported for a small number of systems only [2–7].

Some systems can demonstrate multiple Widom lines. One can expect the appearance of multiple Widom lines in the systems with complex phase diagrams like water. In particular, multiple Widom lines look natural in systems with liquid-liquid phase transitions. According to recent studies, carbon dioxide can also possess very a complex phase diagram which includes molecular, polymeric, and dissociated metallic fluid phases [10]. In addition to the conventional liquid-gas Widom line of CO_2, the Widom line was reported to be related to the transition between molecular and polymeric liquids and was calculated using isothermal compressibility maxima. One might expect that the qualitative behavior of the second Widom line of carbon dioxide will be similar to the behavior of the usual gas-liquid Widom line, although this question requires further study.

Another line dividing a supercritical fluid in two regions, low-temperature "rigid" liquid and high-temperature nonrigid gaslike fluid, was proposed in the literature [11–13]. It was named the Frenkel line. The Frenkel line separates two states with qualitatively different molecular dynamics. In the rigid-liquid regime, the particle motion includes both oscillations around an equilibrium position and gaslike diffusive jumps. In the nonrigid gaslike regime, the oscillatory motion of particles is lost and only gaslike diffusive motion remains.

Here, we report the results of a computational study of supercritical CO_2. We report the thermodynamical properties of CO_2 (equation of state and response functions) and the location of supercritical maxima in the (ρ,T) plane. This particular system was chosen for its importance in the chemical industry and planetary science. We investigate the behavior of the heat capacity, isobaric expansion, isothermal compressibility, and density fluctuations. We also perform a preliminary study of the Frenkel line of carbon dioxide.

II. SYSTEM AND METHODS

We studied the supercritical maxima of CO_2 using molecular dynamics (MD) simulations. The model potential from Ref. [14] was used. This potential was optimized for simulating of the liquid-gas coexistence and gives the saturation curve and the critical point in close agreement with experimental data. In this model, carbon dioxide molecules are considered as rigid bodies, i.e., the C–O bond length and the O–C–O angle are fixed. Each molecule of CO_2 contains three interaction sites: a carbon atom and two oxygens. All three atoms in a molecule interact with atoms of other molecules by LJ and Coulombic forces. The effects of multipole interactions, three-body forces, and the polarizability of the molecules are neglected.

TABLE I. Fitting coefficients for pressure and internal energy. The fitting formula is $X = \sum_{p,q} a_{p,q} \rho^p T^q$, where $X = P$ and U. The densities ranging from 0.2 up to 0.7 g/cm^3 were used for this fit. The units of pressure are bars (1 bar = 10^5 Pa = 0.1 MPa) and the units of energy are Kelvin (1 K = 1.38×10^{-23} J). Temperatures and densities are measured in K and g/cm^3, respectively.

p	q	$a_{p,q}$ for P	$a_{p,q}$ for U
0	0	–59.199	8884.811
1	0	–12.402	–5347.037
2	0	–1889.319	4859.453
3	0	4090.029	823.207
4	0	–7561.170	–1968.605
5	0	3396.4327	286.739
0	1	0.365	16.137
1	1	1.041	18.175
2	1	–3.832	–23.120
3	1	4.0548	2.038
4	1	4.704	2.006
0	2	-4.726×10^{-4}	-4.598×10^{-2}
1	2	7.126×10^{-3}	-2.406×10^{-2}
2	2	7.367×10^{-3}	3.183×10^{-2}
3	2	-5.046×10^{-3}	-3.640×10^{-3}
0	3	-1.354×10^{-6}	7.573×10^{-5}
1	3	-1.093×10^{-5}	9.430×10^{-6}
2	3	-9.953×10^{-7}	-1.315×10^{-5}
0	4	3.128×10^{-9}	5.926×10^{-8}
1	4	4.594×10^{-9}	9.248×10^{-10}
0	5	-1.614×10^{-12}	1.779×10^{-11}

A system of 4000 CO_2 molecules was simulated in a cubic box with periodic boundary conditions in the canonical ensemble (the number of particles N, the volume of the system V, and the temperature T are fixed). The time step was set to $\delta t = 0.1$ fs. A period of 100 ps was used to equilibrate the system, followed by the simulation for 100 more ps in order to compute the averages. These time scales were enough due to high-temperature regimes studied. The system was simulated at the densities from 0.2 g/cm^3 up to 0.7 g/cm^3 with the step $\Delta\rho = 0.025$ g/cm^3. The temperatures studied varied from 310 K up to 400 K with the step $dT = 10$ K and then up to 900 K with the step 20 K. Critical parameters of the model were reported in Ref. [14]: $T_c = 304$ K, $\rho_c = 0.467$ g/cm^3, and $P_c = 7.23$ MPa. Therefore, the pressure and temperature conditions used in our work correspond to the temperatures from slightly above T_c to approximately $3T_c$ and to densities from approximately $0.5\rho_c$ up to almost $3.5\rho_c$. To compute the Frenkel line, we extended the simulations up to the densities $\rho = 1.5$ g/cm^3. Twenty-nine different densities and 35 different temperatures were studied in total, providing a large data set of energies and pressures as functions of ρ and T. We estimate the precision of the simulation data as 2%. These data were fitted to polynomial functions of the form $X = \sum_{p,q} a_{p,q} \rho^p T^q$, where X represents the pressure or the internal energy of the system. The maximal values of p and q were taken as 5. In total the fitting functions contained 21 parameters which allowed high quality fitting with the precision higher than 1%. The fitting parameters for pressure and energy are given in Table I.

The fitting functions described above were used to compute the thermodynamic response functions: density fluctuations $(\frac{\partial\rho}{\partial P})_T$, isothermal compressibility $\chi_T = \frac{1}{\rho}(\frac{\partial\rho}{\partial P})_T$, thermal expansion coefficient $\alpha_P = \frac{1}{\rho}(\frac{\partial\rho}{\partial T})_P$, constant volume heat capacity $c_V = (\frac{\partial E}{\partial T})_V$, and constant pressure heat capacity $c_P = (\frac{\partial H}{\partial T})_P$, where E and $H = E + PV$ are the internal energy and the enthalpy of the system. All simulations were performed using LAMMPS simulation package [15].

III. RESULTS AND DISCUSSION

Several methods to locate the Frenkel line in the (ρ,T) plane or the (P,T) plane were recently discussed [11–13]. The most convenient of them are based on the velocity autocorrelation function and the isochoric heat capacity. Indeed, oscillations of the particle motion in the rigid fluid are easily recognized by the presence of nonmonotonic behavior of the velocity autocorrelation. In the nonrigid gaslike regime, the velocity autocorrelation function monotonically decays to zero. Very recently calculations of Frenkel line of CO_2 by the velocity autocorrelation function criterion were reported in the literature [16].

The heat capacity criterion for the Frenkel line is based on the following reasoning. The heat capacity of the monatomic crystal is equal to $3k_B$ per atom in the classical case and has contributions from one longitudinal and two transverse modes. In a liquid, transverse modes gradually disappear with temperature, in quantitative agreement with the experimental reduction of the specific heat from $3k_B$ at low temperature to $2k_B$ at high temperature [17,18]. The important difference between rigid and nonrigid fluids is that the former can sustain transverse modes (at frequency larger than the inverse liquid relaxation time [19]) while the latter cannot sustain transverse modes at any available frequency up to the maximal Debye frequency. With no transverse modes propagating, the liquid energy per particle includes k_BT from one longitudinal mode and the remaining kinetic terms from two transverse modes ($\frac{1}{2}k_BT$ for each of the two transverse modes) but no contribution from the potential terms, giving the liquid energy per particle of $2k_BT$ and the specific heat $c_v = 2k_B$ [17].

The speculations above consider a monatomic liquid. In the case of CO_2, which consists of rigid molecules, one can easily estimate the heat capacity at the Frenkel line by the following reasoning. It is well known from experiment that the heat capacity of CO_2 close to the triple point is $4.5k_B$. Obviously, at triple point the liquid is rigid and can propagate the transverse modes. At the Frenkel line two transverse modes disappear, reducing the specific heat by twice the kinetic component of each transverse mode ($2 \times \frac{1}{2}k_B$) [17]. As a result one obtains $c_v = 3.5k_B$ at the Frenkel line.

We first report the equations of state of the supercritical carbon dioxide (Fig. 1). Figure 1 shows our MD data compared to the experimental results from the NIST database [20]. One can see that the MD data are in good agreement with experimental results. Figure 1 also demonstrates the polynomial fit of the data. An important conclusion from Fig. 1 is that the results of simulations are in good agreement with experimental results, which justifies the reliability of our study. This means that even if the potential we employ in the present

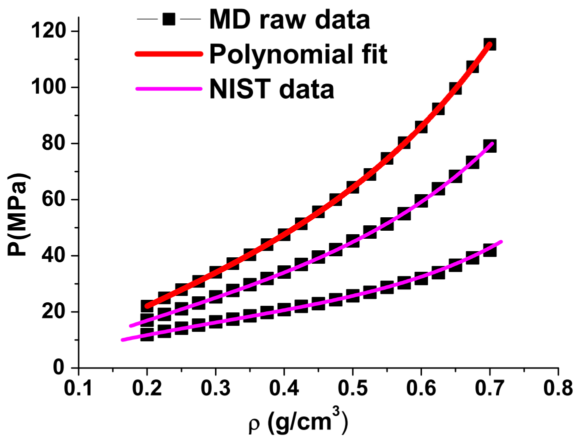

FIG. 1. (Color online) Equation of state of CO_2. The plot shows raw data from MD simulation (symbols), polynomial approximation for $T = 600$ K and experimental data from the NIST database for $T = 400$ K and 500 K. Temperature from bottom to top: 400 K, 500 K, and 600 K.

study [14] were fitted to reproduce the liquid-gas saturation line it could also be successfully used to study the system and analyze its properties in the supercritical region.

Figure 2 shows density fluctuations at a set of temperatures slightly above the critical one. One can see that, at the lowest temperature, there is a well-defined maximum. However, this maximum rapidly decays. The maximum is seen at quite high temperatures (as high as 540 K), but it becomes of the order of numerical errors.

Figure 3 shows the behavior of the isothermal compressibility in the same temperature range. Unlike in the previous case, the maximum quickly vanishes. Even at a temperature as low as 350 K, the maximum is already unobservable.

Figure 4 shows the isochoric heat capacity along the same set of isotherms. As before, we observe well-defined maxima that can be traced to temperatures as high as 440 K.

The behavior of the isobaric heat capacity c_p was studied along both isobars and isotherms. Figure 5 demonstrates that

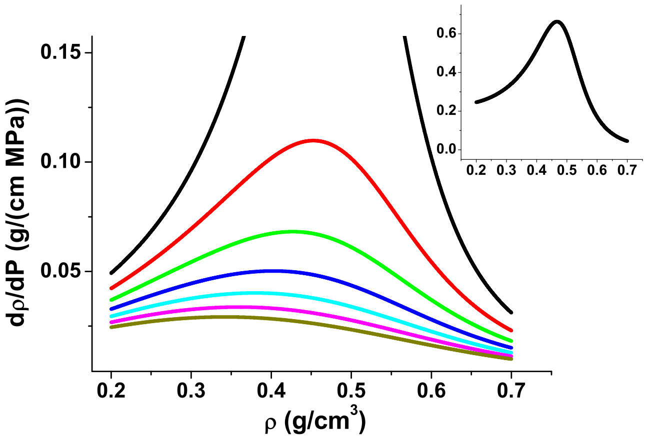

FIG. 2. (Color online) Density fluctuations along several isotherms. The temperatures are from $T = 320$ K (top) up to $T = 380$ K (bottom) with step $\Delta T = 10$ K. The inset enlarges the plot for $T = 320$ K.

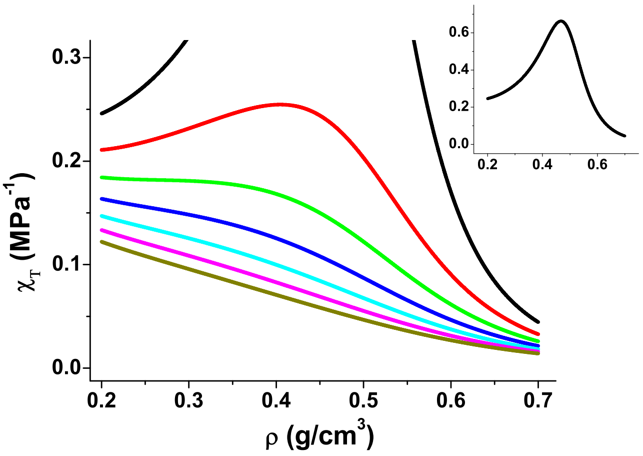

FIG. 3. (Color online) Isothermal compressibility of CO_2 along several isotherms. The notation is the same as that in Fig. 2. The inset enlarges the plot for $T = 320$ K.

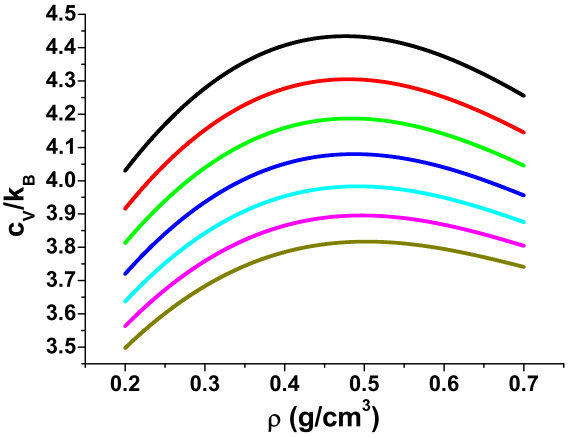

FIG. 4. (Color online) Isochoric heat capacity CO_2 along several isotherms. The notation is the same as that for Fig. 2.

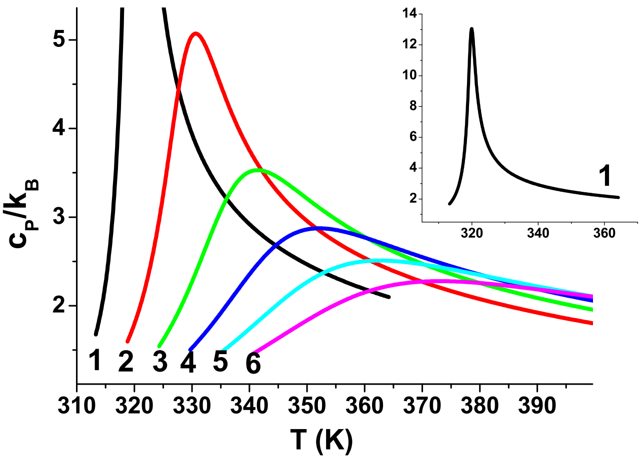

FIG. 5. (Color online) Isobaric heat capacity along a set of isobars. Pressures are from 10 MPa (curve 1) up to 20 MPa (curve 6) with step $\Delta P = 2$ MPa. The inset enlarges the plot for 10 MPa.

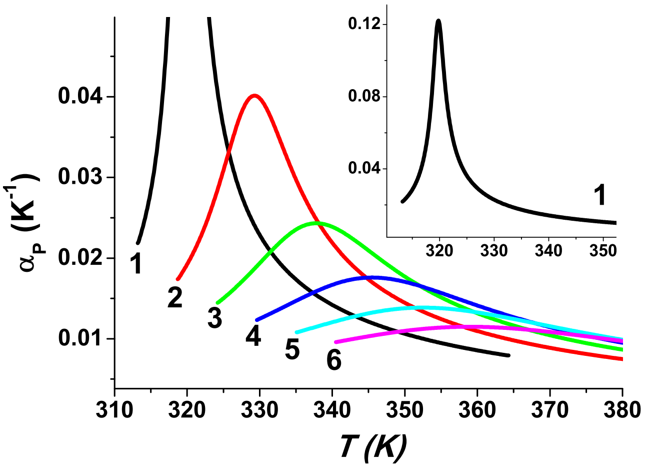

FIG. 6. (Color online) Isobaric expansion coefficient along a set of isobars. Pressures are from 10 MPa (curve 1) up to 20 MPa (curve 6) with step $\Delta P = 2$ MPa. The inset enlarges the plot for 10 MPa.

c_p shows sharp maxima when approaching T_c along the isobars. As the pressure increases, the maximum becomes broader and less pronounced. The maximum can be observed even at pressures up to 100 MPa. However, at such high pressures the maximum becomes of the order of the numerical errors.

The last quantity we study is the isobaric expansion coefficient (Fig. 6). This coefficient was also calculated along both isobars and isotherms. Similarly to c_p, it demonstrates sharp maxima at temperatures close to T_c. These maxima rapidly decrease with increasing pressure. The largest pressure at which we were able to observe the maximum was 44.0 MPa.

The location of the maxima of different quantities is shown in Fig. 7. One can see that the qualitative behavior of different quantities is analogous to the case of the LJ fluid.

Importantly, the fluctuations of density and isothermal compressibility maxima move to the lower densities with increasing temperature, while the maxima of the heat capacities and the isobaric expansion coefficient shift to higher densities at higher temperatures. As a result, the lines of maxima rapidly diverge forming a bunch of lines. For example, already at $T = 320$ K (4% above the critical point) the difference between the densities of maxima of different quantities is as large as approximately 12%. Therefore, the lines of maxima of different quantities fall on the same line in a small temperature range above the critical point only.

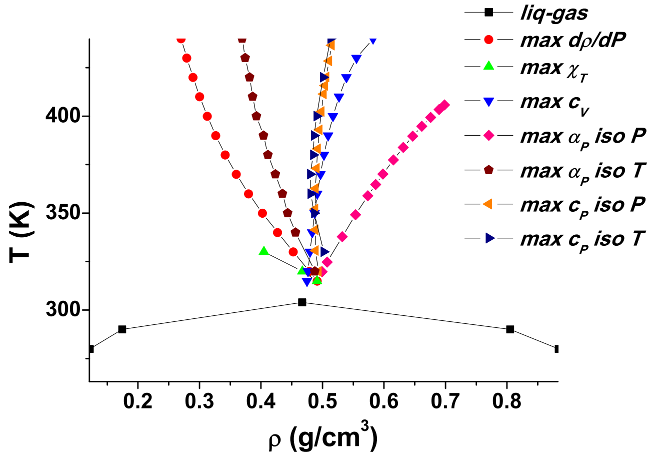

FIG. 7. (Color online) Location of maxima of different thermodynamic functions of CO_2 in the (ρ,T) plane. The liquid-gas coexistence curve is taken from Ref. [14].

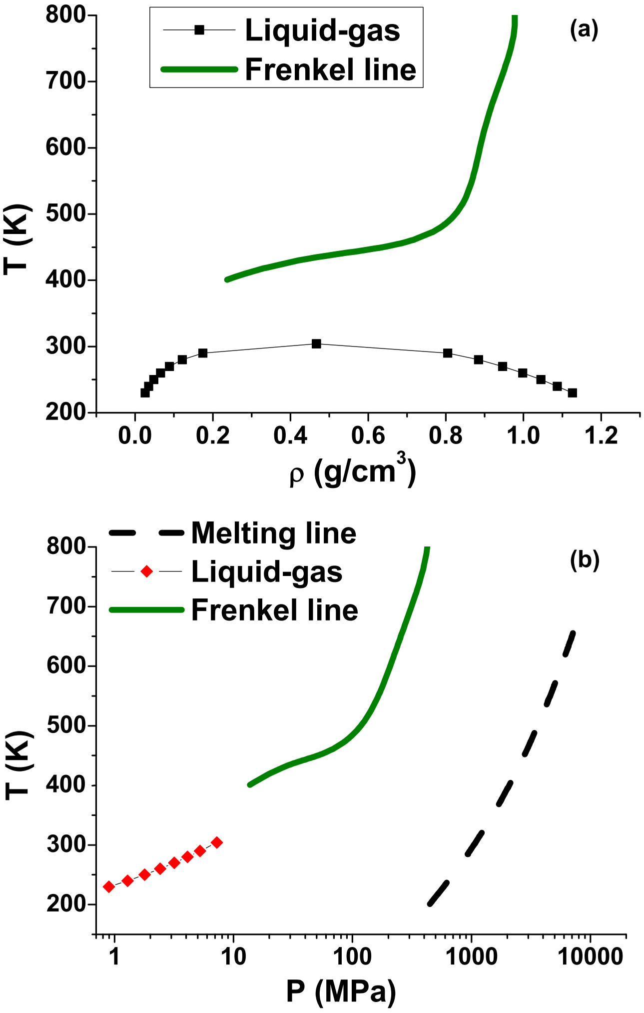

FIG. 8. (Color online) Location of the Frenkel line of CO_2 in (a) (ρ,T) and (b) (P,T) planes.

Of equal importance, we observe that even the maxima of the same quantity taken along different thermodynamic trajectories (isotherms, isochors, isobars) can have different locations. One can see that the maxima of α_P along isotherms and isobars are very different. At the same time, the locations of isothermal and isobaric maxima of c_p are almost identical.

Finally, we report a preliminary estimation of the Frenkel line in CO_2 based on the isochoric heat capacity c_v [11–13] using the data shown in Figs. 8(a) and 8(b) and show the Frenkel line in the (ρ,T) and (P,T) planes. In the case of (P,T) coordinates we also add the experimental melting line from Ref. [21] [Eq. (3)].

One can see from Figs. 8(a) and 8(b) that the Frenkel line calculated using the specific heat criterion bends at relatively low temperature. This bend is related to the supercritical maximum of heat capacity and does not correspond to the dynamic crossover at the Frenkel line. At higher temperature and pressure, the Frenkel line becomes approximately parallel to the melting line in logarithmic coordinates.

Investigation of CO_2 is important for planetary sciences and in particular for understanding the physical processes on Venus. The concentration of carbon dioxide in the atmosphere of Venus is approximately 96%. The current temperature of Venus is estimated to be as high as 735 K, and the atmospheric pressure is estimated to be 9.3 MPa. One can see from Fig. 8(b) that this (P,T) point lies deeply inside the gaslike state above the Frenkel line. However, it is argued in the literature [22] that, at the earlier stages of Venus's evolution, the atmospheric pressure may have been as high as several dozens of MPa. This means that the atmosphere in the early Venus consisted of carbon dioxide in the rigidlike state below the Frenkel line, but has later undergone a transition across the Frenkel line into the nonrigid gaslike fluid. The crossover was accompanied by the microscopic dynamics of the fluid and qualitatively altering many physical properties [11–13], with important implications for forming the landscape of the planet.

IV. CONCLUSIONS

Using MD simulations, we reported the equation of state and supercritical maxima of carbon dioxide and found excellent agreement between simulations and experiments. We showed that similar to model liquids studied before, the lines of supercritical maxima of CO_2 rapidly diverge and form a wide bunch of lines. Furthermore, even the maxima of the same quantity taken along different lines (isotherms or isobars) form different lines. These results justify our earlier conclusion that the concept of the Widom line as the line of supercritical maxima is ill-defined and does not have a clear physical sense [5]. We have calculated the Frenkel line for carbon dioxide and showed that it is approximately parallel to the melting line in logarithmic coordinates, providing a useful guide for estimating the line for other conditions and systems.

ACKNOWLEDGMENTS

We are grateful to K. Trachenko for discussions. Yu.F. thanks the Russian Scientific Center at Kurchatov Institute and Joint Supercomputing Center of Russian Academy of Science for computational facilities. Yu.F., E.Ts., and V.R. are grateful to the Russian Science Foundation (Grant No. 14-12-00820) for the support. V.B. is grateful to the Russian Science Foundation (Grant No. 14-22-00093).

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