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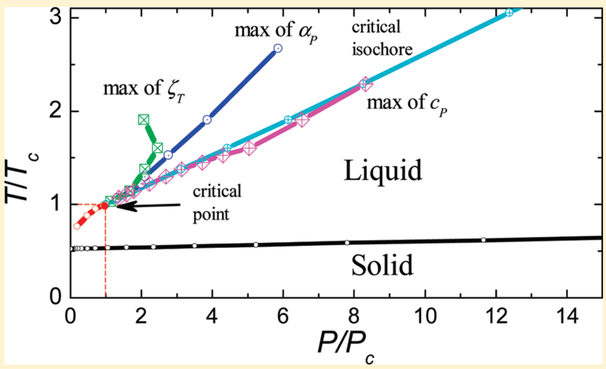
Widom Line for the Liquid−Gas Transition in Lennard-Jones System

V. V. Brazhkin,* Yu. D. Fomin, A. G. Lyapin, V. N. Ryzhov, and E. N. Tsiok

Institute for High Pressure Physics RAS, 142190 Troitsk Moscow Region, Russia

ABSTRACT: The locus of extrema (ridges) for heat capacity, thermal expansion coefficient, compressibility, and density fluctuations for model particle systems with Lennard-Jones (LJ) potential in the supercritical region have been obtained. It was found that the ridges for different thermodynamic values virtually merge into a single Widom line at $T < 1.1T_c$ and $P < 1.5P_c$ and become practically completely smeared at $T < 2.5T_c$ and $P < 10P_c$, where T_c and P_c are the critical temperature and pressure. The ridge for heat capacity approaches close to critical isochore, whereas the lines of extrema for other values correspond to density decrease. The lines corresponding to the supercritical maxima for argon and neon are in good agreement with the computer simulation data for LJ fluid. The behavior of the ridges for LJ fluid, in turn, is close to that for the supercritical van der Waals fluid, which is indicative of a fairly universal behavior of the Widom line for a liquid−gas transition.



INTRODUCTION

The term "fluid" is used to refer to such state of a substance that does not retain its shape and unifies liquid and gas. A liquid−gas phase equilibrium curve in the T,P plane ends at the critical point. At pressures and temperatures above critical ones ($P > P_c$ and $T > T_c$), the properties of a substance in the isotherms and isobars vary continuously, and it is commonly said that the substance is in its supercritical fluid state, when there is no difference between liquid and gas. From the physical point of view, of prime interest is a P,T region near the critical point, where anomalously strong temperature and pressure dependences of most physical quantities (the so-called critical behavior) are observed.[1] Research into the properties of fluids in recent years has also been boosted by broad commercial use of "supercritical" technologies.[2]

Despite the fact that the properties of the supercritical fluid under changes of parameters vary continuously, an anomalous behavior of the majority of thermodynamic characteristics is observed in the vicinity of the critical point. At the critical point, the correlation length for thermodynamic fluctuations diverges;[1] in the vicinity of the critical point, one can observe a critical behavior of physical values determined by the second derivatives of the Gibbs thermodynamic potential, for instance, for the compressibility coefficient β_T, thermal expansion coefficient α_P, and heat capacity c_P: the given properties pass through their maxima under a change of pressure or temperature. Near the critical point, all of these values are proportional to the power function of the correlation length, and the positions of the maxima of the given characteristics in the T,P plane are close together.[1] The same is true for the value of density fluctuations, the speed of sound, thermal conductivity, and so on. Thus, in the supercritical region, there is a whole set of the lines of extrema of various thermodynamic values. Each of these lines can be regarded as a continuation of the liquid−gas phase equilibrium curve into the supercritical region. Smearing and decreasing (in magnitude) extrema of each of the values form a "ridge".[3−5] A knowledge of the positions of the above ridges in the T,P plane is very important; in particular, this knowledge determines a maximum value for such technologically essential characteristics as the dissolving ability of a supercritical fluid, the rate of chemical reactions in a fluid, and others (refs 2−5 and refs therein). It turned out that the experimentally observed lines of the ridges are close to an critical isochoric lines with a slight decrease in density with increasing temperature.[3−5] Most studies on the supercritical region focused on examining the ridge for the density fluctuations.[3,5]

H. E. Stanley suggested that the line of the maxima of the correlation length along the isotherms should be named the "Widom line".[6] Because the lines of the maxima near the critical point merge into one line, the above term was proposed to be used in a wider sense, in reference to the lines of the maxima of all values determined by the second derivatives of the Gibbs thermodynamic potential. The Widom lines for both liquid−gas and liquid−liquid transitions for a number of systems with different interparticle potentials were obtained both analytically and from computer simulation data.[6−10] At the same time, most works on the analysis of the Widom line have been concerned with a liquid−liquid transition for water. The Widom line for a liquid−gas transition is less carefully studied. The Widom line, being a continuation of the boiling curve, in fact, separates a

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liquid-like fluid from a gas-like fluid. It is a priori unclear how far from the critical point we may speak of a single Widom line for all ridges and how far from the critical point the extrema of particular physical quantities can still be followed.

In this work, we have calculated the lines of maxima of different physical values in the supercritical region for a system of particles with a Lennard-Jones (LJ) potential. It is well known that the LJ potential adequately represents the behavior of molecular and rare gas liquids. Thermodynamic and kinetic properties of the LJ particle system have been studied via computer simulation in hundreds of works. For example, the thesis[11] presented the summed up data of many works on the computation of such properties of the LJ system as the equation of state, internal energy, heat capacity at constant volume, and others in over hundred P,T points. However, any systematic analysis of the behavior of thermodynamic properties in the supercritical region has not previously been conducted. A comparison between the results obtained for the LJ fluid and those obtained for the van der Waals fluid is also of interest because in the latter case there are exact analytical expressions for all values.

METHODS

We have studied LJ liquid in a very wide range of parameters. System size varied depending on the density reaching 4000 particles at the highest densities. The cutoff radius was set to 2.5σ. The contribution of the particles beyond this cutoff was estimated with the usual density dependent tail corrections. The equations of state were integrated by velocity Verlet algorithm. The temperature was kept constant during the equilibration by velocities rescaling. When the equilibrium was reached, the system was simulated in NVE ensemble. The usual equilibration period was 1.5 million steps, and the production run was 0.5 million steps, where the time step $dt = 0.001$ LJ units. (The unit of time is $\sigma(m/\varepsilon)^{1/2}$.)

To calculate the Widom line, defined as continuation of the boiling line using the points of thermodynamic maxima, we calculated maxima of the following quantities: isobaric heat capacity c_P, isothermal compressibility $\beta = 1/\rho(\partial\rho/\partial P))_T$, isobaric heat expansion $\beta = 1/\rho(\partial\rho/\partial T)_P$, and density fluctuations $\langle\Delta N^2\rangle/\langle N\rangle = T(\partial\rho/\partial P)_T = \varsigma_T$. The maxima of all of these quantities rapidly decay with increasing temperature. Three quantities (β_T, ζ_T, and α_P) were computed by numerical differentiation of equation of states. Using the data of potential energy and equation of state for LJ fluid from ref 11, we calculated the enthalpy along isobars and correspondingly isobaric heat capacity c_P. The interpolation method was used to find the maximum of c_P. For the van der Waals fluid, the analytical expressions for all four values β_T, α_P, c_P, and $(\partial\rho/\partial P)_T$ have been obtained, and the lines of the respective maxima have been drawn. The experimental data for real fluids have been taken from ref 12.

RESULTS AND DISCUSSION

We have calculated the behavior of the maxima β_T, α_P, c_P, and $(\partial\rho/\partial P)_T$. The results are summarized in Figure 1a,b. Although all ridges are described by different equations, they are close together near the critical point. For the estimate, the lines of the extrema can be thought of as coinciding if the temperature values on the different lines on the isobar differ by <1%. The value of 1% roughly corresponds to the experimental accuracy of

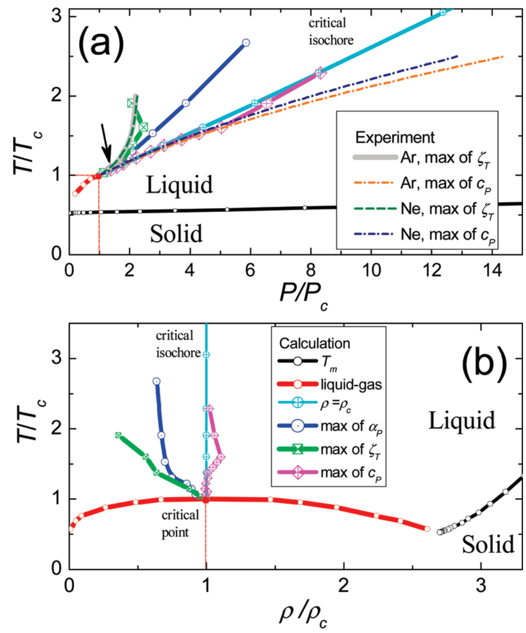

Figure 1. (T,P) and (T,ρ) phase diagrams of the simulated LJ liquid with the calculated lines of maxima for thermal expansion α_P, fluctuations ζ_T, and isobaric thermal capacity c_P. These lines are terminated according to the criterion in the text. The arrow indicates the approximate end of the single Widom line. The experimental lines of maxima for ζ_T and c_P for Ar and Ne[12] are also shown in panel a. All notations for the calculated lines are the same in the both panels.

a measurement of the respective values and to the errors in the computer simulation data. For LJ fluid, the positions of all ridges for different thermodynamic values merge into single Widom line in the P,T coordinates only at $T < 1.1T_c$ and $P < 1.5P_c$. (See the arrow in Figure 1a.)

As the temperature and pressure increase, the maxima of all values rapidly decrease and become smeared (Figures 2 and 3). As a conditional criterion of actual disappearance of the extremum, one can consider the ratio of a respective thermodynamic value in the maximum to this value at densities being 10% different from the density in the extremum. If this ratio is <1.01 (the difference between the maximum value and the "background" value is below 1%), then the ridge can be thought of as actually smeared. When using the above criterion, the lines of all extrema, in fact, end at rather moderate temperatures

$$T \approx 2T_c \quad \text{for} \quad \zeta_T$$

$$T \approx 2.8T_c \quad \text{for} \quad \alpha_P$$
$$T \approx 2.5T_c \quad \text{for} \quad c_P$$

Because the line for maxima of β_T ends very close to critical point, this line is not shown in Figure 1. Figure 1 also displays the experimental position of the maxima for c_P and $(\partial\rho/\partial P)_T$ for argon and neon according to the data given in ref 12, it can be seen that the lines corresponding to the supercritical maxima for argon and neon are in good agreement with the computer simulation data. Most lines correspond to a decrease in the density with increasing temperature; only the line of maxima of the heat capacity c_P lies close to the critical isochore and slightly deviates to a higher density side at $T > (1.5-2)T_c$.

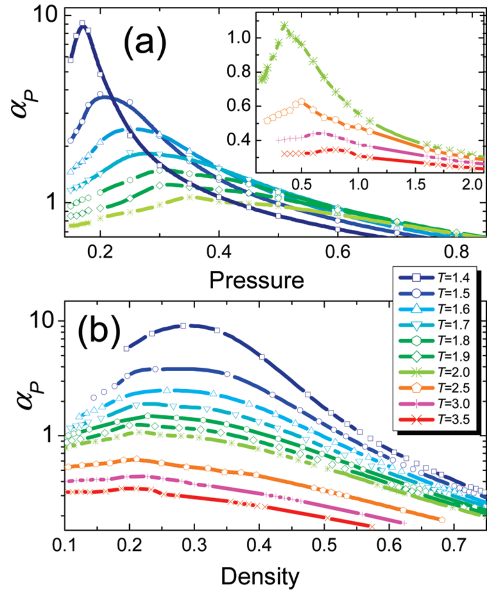

Figure 2. Isothermal pressure (a) and density (b) dependences of thermal expansion α_P for supercritical LJ fluid are presented in LJ units ($\rho_c = 0.314$ and $T_c = 1.31$). The high-temperature curves in panel a are put into the inset. The temperature notations are the same in both panels.

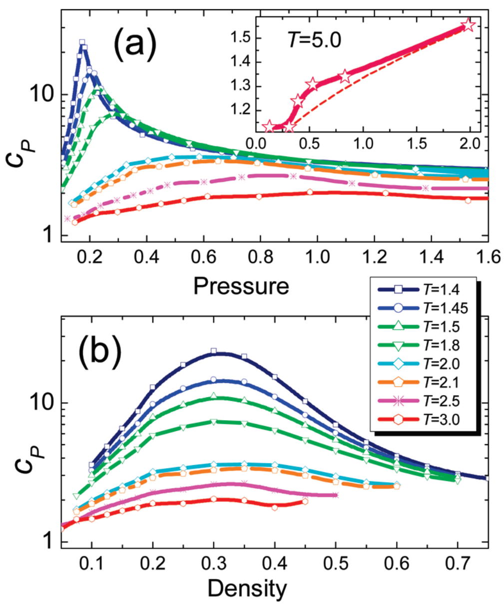

Figure 3. Isothermal pressure (a) and density (b) dependences of isobaric thermal capacity c_P are presented in LJ units ($\rho_c = 0.314$ and $T_c = 1.31$). The temperature notations are the same in the both panels. The inset in panel a shows an example of high-temperature curve, when maximum can not be determined.

Therefore, a "thermodynamic" continuation of the gas−liquid phase equilibrium line for a LJ fluid represents a single Widom line if the temperature moves only 10% away from the critical point; if the temperature moves further away, it represents a rapidly widening bunch of lines. This bunch adjoins the critical isochore on its low density side and ends at $T<(2.5-3)T_c$ and $P < (10-20)P_c$.

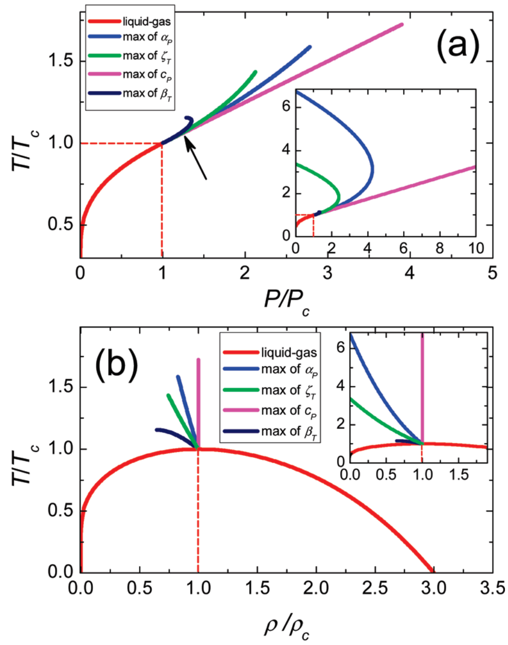

Figure 4. (T,P) and (T,ρ) phase diagrams of the simulated van der Waals fluid with the lines of maxima for thermal expansion α_P, fluctuations ζ_T, isobaric thermal capacity c_P, and compressibility β_T. These lines are terminated according to the criterion in the text. The arrow indicates the approximate end of the single Widom line. The insets show the full pictures of these line calculated using analytical expressions.

The maximum correlation length line is inside the above bunch, too. It is commonly suggested that the isotherms of the correlation length behave like those of the density fluctuations.[3] The correlation length ξ is related to the density fluctuations and determined from the expression[1]

$$\langle (\rho(0) - \rho)(\rho(r) - \rho) \rangle \sim \frac{exp(-r/\xi)}{r}$$

A complex volume dependence of the ξ value cannot be obtained analytically and is strongly dependent on the used approximations. The variation with density of the locus of maxima of the value ξ on the isotherms is still more sensitive to the used approximations and their self-consistency procedure. For all such approximations, the line of the maxima of the value ξ lies within the bunch of other lines and, in fact, ends at $T < (2-3)T_c$.

It is of interest to compare the data on the lines of supercritical anomalies for the LJ fluid with the respective analytical results for a fluid with a model equation of state, for instance, the van der Waals fluid. The data on the lines of the maxima of thermodynamic values for the van der Waals fluid are given in Figure 4. A criterion for the merge of all lines into a single Widom line and the criterion for the virtual disappearance of the maxima were chosen to be the same as for the LJ fluid. The positions of all lines for different thermodynamic values merge into single Widom line only at $T < 1.07T_c$ and $P < 1.25P_c$. (See the arrow in Figure 4a.) Formally, the line of the maxima of density fluctuations and that of the maxima of thermal expansion coefficient for a van der Waals fluid formally go until zero pressures, and the line of the maxima of heat capacity goes to an infinite temperature region at all. (See the insets in Figure 4.) However, the amplitude of all extrema very rapidly decays if we move away from the critical point. When using the same criterion, the lines of all extrema, in fact, end at a relatively small distance away from the critical point

$$T \approx 1.15T_c \quad \text{for} \quad \beta_T$$
$$T \approx 1.5T_c \quad \text{for} \quad \zeta_T$$
$$T \approx 1.6T_c \quad \text{for} \quad \alpha_P$$
$$T \approx 1.7T_c \quad \text{for} \quad c_P$$

As in the case of the LJ fluid in the van der Waals model, the lines of the maxima of most values correspond to a decrease in density with increased temperature; only the line of the maxima of the heat capacity c_P lies on the critical isochore (Figure 4b). In the study,[3] it was supposed that the reason why the lines of the maxima of density fluctuations and correlation length correspond to a decrease in density is an increase in the effective volume occupied by molecules with an increase in temperature.

The fact that the Widom line and the lines of the maxima of heat capacity lie virtually exactly on the critical isochore is obviously true for the majority of fluids. A small deviation of the line of the maximum of c_P to a larger density at high temperatures for the LJ fluid and real fluids Ar and Ne (Figure 1) is associated with the increase in c_P with pressure far away in the supercritical region. (See the inset in Figure.3a.) As a result, the position of a smeared maximum of a small value effectively displaces to the side of larger pressures (densities) merely for mathematical reasons.

CONCLUSIONS

In summary, one can conclude that the single Widom line lies almost on the critical isochore and ends if one moves 10% away from the critical temperature. If one moves further away from the critical point, the line of maxima for all thermodynamic values rapidly diverge from one another, and the maxima themselves become quickly smeared and virtually disappear at temperatures $(2.5-3)T_c$.

A similarity in the behavior of the lines of supercritical anomalies for the LJ and van der Waals fluids suggests that the obtained qualitative results will be valid for all liquid−gas transitions. At the same time, a single Widom line and individual lines of the maxima for the LJ fluid can be followed when one moves 1.5 to 2 times away longer from the critical point as compared with those for the van der Waals fluid. The results for the lines of supercritical anomalies for a liquid−liquid transition[9,10] indicate that the quantitative results of the behavior of the of ridges are fairly sensitive to the type of potential, too. In any case, however, at sufficiently high pressures ($P_c > 20$), it is dynamic, not thermodynamic, characteristics that should be considered when separating a fluid into liquid- and gas-like regions.

AUTHOR INFORMATION

Corresponding Author

*E-mail: brazhkin@hppi.troitsk.ru.

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