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True Widom line for a square-well system

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In the present paper we propose a van der Waals–like model that allows a purely analytical study of fluid properties including the equation of state, phase behavior, and supercritical fluctuations. We take a square-well system as an example and calculate its liquid-gas transition line and supercritical fluctuations. Employing this model allows us to calculate not only the thermodynamic response functions (isothermal compressibility β_T, isobaric heat capacity C_P, density fluctuations ζ_T, and thermal expansion coefficient α_T), but also the correlation length in the fluid ξ. It is shown that the bunch of extrema widens rapidly upon departure from the critical point. It seems that the Widom line defined in this way cannot be considered as a real boundary that divides the supercritical region into gaslike and liquidlike regions. As it has been shown recently, a dynamic line on the phase diagram in the supercritical region, namely, the Frenkel line, can be used for this purpose.

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In recent years, increasing attention has been given to the investigation of properties of supercritical liquids. This interest is mainly due to the fact that supercritical fluids are widely used in industrial processes. Their behavior away from the critical point is therefore an important practical question because it might affect their applicability in the considered technological process [1]. Theoretical aspects of the physics of supercritical fluid are of particular interest as well.

The liquid-gas phase equilibrium curve in the P-T plane ends at the critical point. At pressures and temperatures above the 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 a physical point of view, the P-T region near the critical point, where anomalous behavior of the majority of characteristics is observed (the so-called critical behavior), is of prime interest [2]. The correlation length of thermodynamic fluctuations diverges at the critical point [2]. One can also observe a critical behavior of the thermodynamic response functions, which are defined as second derivatives of the corresponding thermodynamic potentials, such as the compressibility coefficient β_T, thermal expansion coefficient α_P, and heat capacity C_P. These quantities pass through their maxima during pressure or temperature variations and diverge as the critical point is approached. Near the critical point, the positions of the maxima of these values in the T-P plane are close to each other. The same is true for the density fluctuations, speed of sound, thermal conductivity, etc. Therefore, in the supercritical region, there is a whole set of the lines of extrema of various thermodynamic parameters. The lines of the maxima for different response functions asymptotically approach one another as the critical point is approached because all response functions can be expressed in terms of the correlation length. This asymptotic line is sometimes called the Widom line and is often regarded as an extension of the coexistence line into the one-phase region [3]. The Widom lines for the gas-liquid and liquid-liquid phase transitions have been investigated extensively [3–14].

Because of the lack of a theoretical method for constructing the Widom line, based on the extremum of the correlation length, the locus of extrema of the constant-pressure specific heat C_P was often used as an estimation for the Widom line. In Refs. [9,11], using computer simulations, the locus of extrema (ridges) for the heat capacity, thermal expansion coefficient, compressibility, and density fluctuations for model particle systems with the 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 almost completely smeared at $T < 2.5T_c$ and $P < 10P_c$, where T_c and P_c are the critical temperature and pressure. The analytical expressions for the extrema of the heat capacity, thermal expansion coefficient, compressibility, density fluctuation, and sound velocity in the supercritical region were obtained in Refs. [10,11] in the framework of the van der Waals (vdW) model. It was found that the ridges for different thermodynamic values virtually merge into a single Widom line only at $T < 1.07T_c, P < 1.25P_c$ and become smeared at $T < 2T_c, P < 5P_c$. However, in both of the studies, the estimation of the Widom line is unsatisfactory because it is *a priori* unclear how far from the critical point the lines of extrema of response functions follow the exact Widom line, determined by the maximum of the correlation length.

Recently, construction of the Widom line by using the approach based on Riemannian geometry was proposed [13]. Previously it was supposed that there is a relation between the Riemannian thermodynamic scalar curvature R of the thermodynamic metric and the volume of the correlation length ξ, i.e., $|R| \propto \xi^3$ [15]. Consequently, the locus of the maximum of $|R|$ describes the locus of the Widom line. In Ref. [13] this approach was applied to a vdW fluid, while in [14] it was used to construct the Widom line for the LJ fluid. It should be mentioned that the location of the lines of the corresponding maxima depends on the trajectory in the space of the thermodynamic parameters (along isotherms, isobars, isochors, etc) [14].

It is of great interest to develop a simple vdW-like model that can represent a liquid-gas transition and the Widom line and can be solved analytically. In this case it would be possible to analyze the relation between the true Widom line, determined from the correlation function, and the lines of extrema of response functions.

We define the model using the approximation for the direct correlation function [16] of the hard-core system, suggested by Lovett [17] (see also [18–20]):

$$c(r) = \begin{cases} c_{\mathrm{HS}}(r), & r \leqslant d \\ -\frac{\phi(r)}{k_B T}, & r > d, \end{cases} \tag{1}$$

where $c_{\mathrm{HS}}(r)$ is the hard-sphere direct correlation function and $\phi(r)$ is the attractive part of the potential. This should be a good approximation when $-\frac{\phi(r)}{k_B T}$ is small. The approximation, though rough, is similar in spirit to the mean spherical model approximation, which has been found to be a good approximation in many cases [16]. Such an approximation formulated directly in terms of $c(r)$ is particularly convenient for the formulation of the Widom line, as it will be shown below. This approximation is especially convenient for direct calculation of the correlation length in the fluid ξ.

Although the method we use is a general tool for liquids, we consider the so-called square-well (SW) system as more specific. One can easily generalize the results to other systems. The square-well system is a system of particles interacting via the following potential:

$$\Phi(r) = \begin{cases} \infty, & r \leqslant d \\ -\varepsilon, & d < r \leqslant \sigma \\ 0, & r > \sigma. \end{cases} \tag{2}$$

Although this system is not very realistic, it can serve as a generic example of a simple liquid. Below we consider the SW system with $\sigma = 1.35d$. In this case, Eq. (1) has the form

$$c(r) = \begin{cases} c_{\mathrm{HS}}(r), & r \leqslant d \\ \frac{\varepsilon}{k_B T}, & d < r \leqslant \sigma \\ 0, & r > \sigma. \end{cases} \tag{3}$$

We use the Percus-Yevick approximation [16,21] for c_{HS}:

$$c_{\mathrm{HS}}(r) = -\lambda_1 - \pi\rho\lambda_2 r - \frac{\pi}{12}\rho\lambda_1 r^3, \tag{4}$$

where

$$\lambda_1 = \frac{(1+2\eta)^2}{(1-\eta)^4}$$

and

$$\lambda_2 = \frac{-d^2(1+1/2\eta)^2}{(1-\eta)^4},$$

with η the packing fraction $\eta = \frac{\pi}{6}\rho d^3$. The direct correlation function can be used to obtain the isothermal compressibility

$$\frac{1}{k_B T}\left(\frac{\partial P}{\partial \rho}\right)_T = 1 - \rho \int d\mathbf{r}\, c(r). \tag{5}$$

Taking into account that the system is isotropic, using Eq. (4) one obtains

$$\frac{1}{k_B T}\left(\frac{\partial P}{\partial \rho}\right)_T = \lambda_1 - \frac{8\varepsilon}{k_B T}\eta\Delta, \tag{6}$$

where $\Delta = (\sigma^3 - d^3)/d^3$.

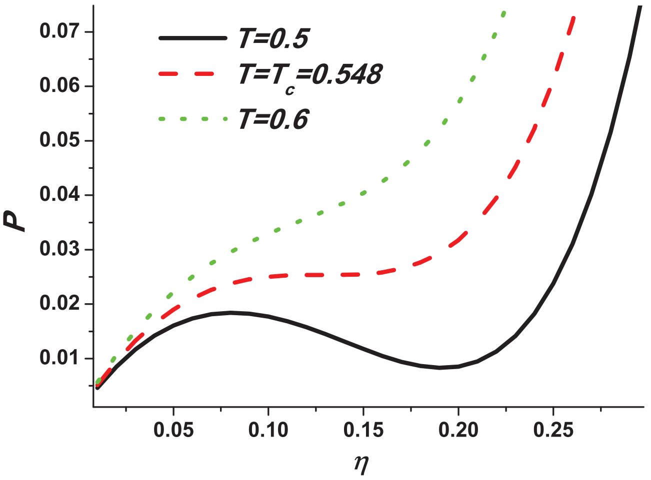

FIG. 1. (Color online) Three isotherms for the SW system: below the critical temperature T_c, at $T = T_c$, and above T_c.

The integration of Eq. (6) gives the equation of state (EOS) for the SW system:

$$\tilde{P} = \tilde{T}\frac{\eta + \eta^2 + \eta^3}{(1-\eta)^3} - 4\Delta\eta^2, \tag{7}$$

where $\tilde{P} = P\frac{\pi d^3}{6\varepsilon}$ and $\tilde{T} = k_B T/\varepsilon$. Later in the paper we will use only these scaled units, omitting the tilde mark. Equation (7) has the form of the generalized van der Waals equation [16,21], where the first part corresponds to the hard-sphere equation of state in the Percus-Yevick approximation and the second part is the van der Waals term.

Figure 1 shows three isotherms for the SW system: below the critical temperature T_c, at $T = T_c$, and above T_c. The critical point can be determined from the following conditions:

$$\frac{\partial P}{\partial \eta} = T\frac{(1+2\eta)^2}{(1-\eta)^4} - 8\Delta\eta = 0 \tag{8}$$

and

$$\frac{\partial^2 P}{\partial \eta^2} = T\frac{8 + 20\eta + 8\eta^2}{(1-\eta)^5} - 8\Delta = 0. \tag{9}$$

Rewriting these equations in the form

$$\begin{aligned} T(1 + 4\eta + 4\eta^2) &= 8\Delta\eta(1-\eta)^4 \\ T(8 + 20\eta + 8\eta^2) &= 8\Delta(1-\eta)^5, \end{aligned} \tag{10}$$

we obtain the following equation for the critical packing fraction:

$$1 - 5\eta - 20\eta^2 - 12\eta^3 = 0. \tag{11}$$

From this equation one can get the critical packing fraction $\eta_c = 0.128\,67\ldots$. The other two roots of Eq. (11) are negative and therefore unphysical. It is important to emphasize that in the approximation (3) the critical density is fully determined by the hard-core diameter d and does not depend on the well width σ.

For the critical temperature one obtains

$$T_c = \frac{8\Delta\eta_c(1-\eta_c)^4}{(1+2\eta_c)^2}. \tag{12}$$

Using the value for the critical packing fraction obtained above, one can write $T_c = 0.375\,312\Delta$. For the system with $\sigma = 1.35d$, which we study here, $T_c = 0.548$. The liquid-gas (LG) transition line can be obtained by the Maxwell construction. [Figures 4(a) and 4(b) show the LG curve in the η-T and P-T planes.]

It is well known that close to the critical point, many thermodynamic functions have maxima. Here we calculate the locations of maxima of different thermodynamic functions in the framework of the method employed. The real advantage of this method is that it allows us to calculate the correlation length ξ, i.e., we are able to compare all the definitions of the Widom line in framework of the purely analytical study of the same system.

The isothermal compressibility is defined as $\beta_T = -\frac{1}{V}(\frac{\partial V}{\partial P})_T$. Rewriting it in terms of η, one obtains

$$\beta_T = \frac{1}{\eta}\left(\frac{\partial \eta}{\partial P}\right)_T = \frac{1}{\eta}\frac{(1-\eta)^4}{T(1+2\eta)^2 - 8\Delta\eta(1-\eta)^4}. \qquad (13)$$

Thermodynamically, the density fluctuation $\zeta_T = (\langle N^2\rangle - \langle N\rangle^2)/\langle N\rangle$ is given by [2]

$$\zeta_T = \frac{\langle N^2\rangle - \langle N\rangle^2}{\langle N\rangle} = T\eta\beta_T. \qquad (14)$$

From Eq. (14) one can see that the density fluctuation is defined as $\zeta_T = T(\frac{\partial\eta}{\partial P})_T$. From the equations given above we have

$$\zeta_T = T\left(\frac{\partial \eta}{\partial P}\right)_T = \frac{T(1-\eta)^4}{T(1+2\eta)^2 - 8\Delta\eta(1-\eta)^4}. \qquad (15)$$

Figure 2(a) shows the density fluctuations along several isotherms. The ζ_T maxima along isotherms are determined from

$$T = \frac{2\Delta(1-\eta)^5}{2+5\eta+2\eta^2}. \qquad (16)$$

Figure 2(b) shows the compressibilities β_T along several isotherms. The corresponding maxima are obtained from

$$T = \frac{16\Delta\eta(1-\eta)^5}{1+11\eta+20\eta^2+4\eta^3}. \qquad (17)$$

The heat capacity C_P can be calculated from the formula

$$C_P - C_V = -T\frac{\left(\frac{\partial P}{\partial T}\right)_V^2}{\left(\frac{\partial P}{\partial V}\right)_T}. \qquad (18)$$

In terms of η this formula is

$$C_P - C_V = \frac{T(1+\eta+\eta^2)^2}{(1-\eta)^2[T(1+2\eta)^2 - 8\Delta\eta(1-\eta)^4]}. \qquad (19)$$

Some examples of the heat capacities along isotherms are shown in Fig. 2(c). The corresponding maxima can be calculated from

$$T = \frac{4\Delta(1-\eta)^4(-1+8\eta+8\eta^2+3\eta^3)}{3\eta(2+5\eta+2\eta^2)}. \qquad (20)$$

Taking into account that, as in the case of the vdW model [2], C_V above the critical point is equal to the ideal gas value, Eq. (20) corresponds to the line of the supercritical maxima of C_P. However, in contrast to the vdW model, where the line

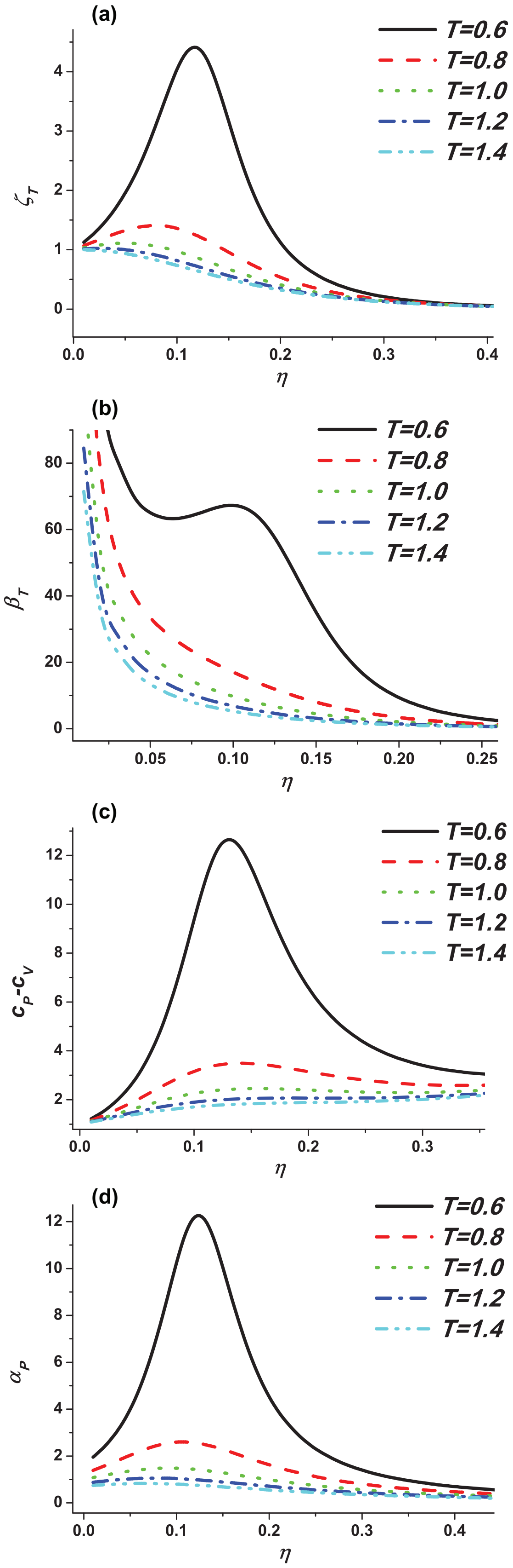

FIG. 2. (Color online) (a) Density fluctuations ζ_T, (b) isothermal compressibility β_T, (c) heat capacity c_P, and (d) isobaric thermal expansion coefficient α_P along several isotherms.

of C_P maxima is located along the critical isochor [10], in this model the supercritical behavior of C_P [see Fig. 2(c)] is similar to that in the case of the LJ fluid [9,14].

The isobaric thermal expansion coefficient is $\alpha_P = -\frac{1}{V}(\frac{\partial V}{\partial T})_P$. Using the EOS (7), one obtains

$$\alpha_P = \frac{1}{\eta}\left(\frac{\partial \eta}{\partial T}\right)_P = \frac{(1+\eta+\eta^2)(1-\eta)}{T(1+2\eta)^2 - 8\Delta\eta(1-\eta)^4}. \tag{21}$$

Some examples of the α_P behavior along isotherms are shown in Fig. 2(d). The corresponding isothermal maxima are given by

$$T = \frac{-8\Delta(1-\eta)^4(-1+4\eta+4\eta^2+2\eta^3)}{4+8\eta+3\eta^2+8\eta^3+4\eta^4}. \tag{22}$$

The correlation length can be calculated in the following way [16]:

$$\xi^2 = \frac{R^2}{1-\rho\tilde{C}_0(T)}, \tag{23}$$

where

$$R^2 = \frac{\rho}{6}\int c(r)r^2 d\mathbf{r} \tag{24}$$

and

$$\tilde{C}_0(T) = \int c(r) d\mathbf{r}. \tag{25}$$

Using the formulas for the direct correlation function [16], one can write

$$1-\rho\tilde{C}_0(T) = \lambda_1 - \frac{8\eta\Delta}{T}. \tag{26}$$

Substituting this equation into the one for R^2, one obtains

$$R^2 = \frac{\eta d^2}{20}\left[\frac{-16+11\eta-4\eta^2}{(1-\eta)^4} + \frac{16\Delta'}{T}\right] \tag{27}$$

where $\Delta' = (\sigma^5 - d^5)/d^5$. Finally, for the correlation length one obtains

$$\tilde{\xi}^2 = \frac{\xi^2}{d^2} = \frac{1}{20}\frac{T(-16\eta+11\eta^2-4\eta^3)+16\eta\Delta'(1-\eta)^4}{T(1+2\eta)^2-8\Delta\eta(1-\eta)^4}. \tag{28}$$

Examples of the correlation length along several isotherms are given in Fig. 3. The maxima of the correlation length at constant T can be calculated as the solutions of

$$\begin{aligned} &4\Delta\eta^2(1-\eta)^3(-53+25\eta-8\eta^2) \\ &+8\Delta'(1-\eta)^3(-1+5\eta+20\eta^2+12\eta^3) \\ &+T(8-11\eta-48\eta^2+16\eta^3+8\eta^4) = 0. \end{aligned} \tag{29}$$

Figure 4(a) shows the LG curve and the points of maxima of all the quantities described above. One can see that the curves of maxima of different thermodynamic functions quickly diverge and even rather close to the critical point, one cannot consider the location of the maxima as a single curve. They actually represent a bunch of curves in the η-T plane. In particular, one can see that the correlation length maxima are located between the α_P and C_P maxima and even the qualitative behavior of the maxima of correlation length is opposite to that of the heat capacity in the η-T plane.

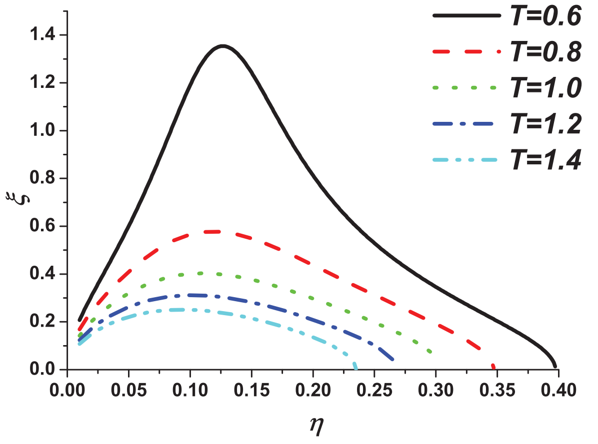

FIG. 3. (Color online) Correlation length ξ along several isotherms.

In Fig. 4(b) the behaviors of maxima of the isothermal compressibility β_T, isobaric heat capacity C_P, density fluctuations ζ_T, thermal expansion coefficient α_T, and correlation length ξ at constant temperature are shown in the P-T plane. One can see again that the bunch of ridges merges into a single line in the very vicinity of the critical point and widens rapidly upon

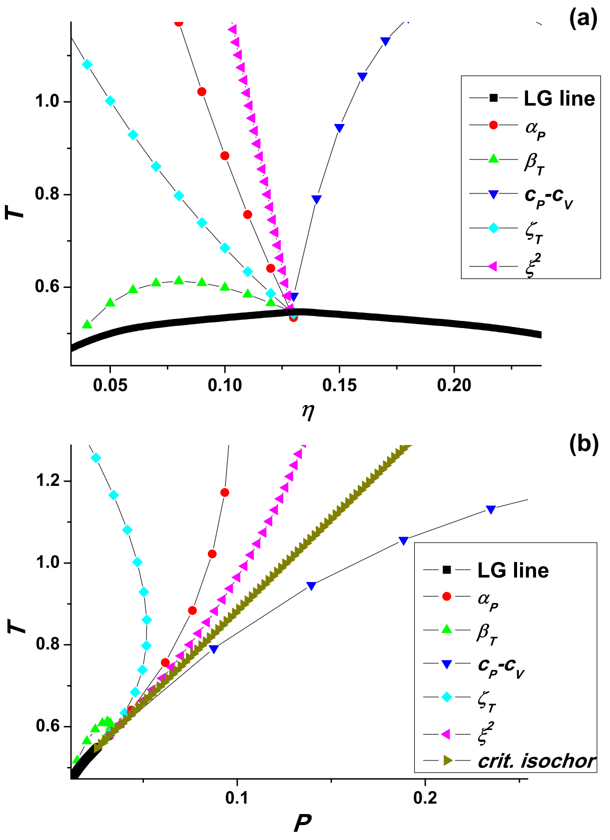

FIG. 4. (Color online) Location of maxima of different thermodynamic quantities close to the LG curve in the (a) η-T and (b) P-T planes.

departure from the critical point. If the Widom line is defined with the help of the correlation function ξ, then the Widom line will not follow the slope of any response function extrema, except in the very close vicinity of the critical point.

It is interesting to note that the sequence of the ξ, β_T, C_P, ζ_T, and α_T extrema in Fig. 4 is the same as the corresponding sequence for the vdW and LJ fluids [9,10,14]. It seems that the similar behavior of the line of the correlation length maxima in our model and the corresponding lines obtained in [14] may be considered as evidence of the universality of a particular location of the true Widom line.

It seems that the Widom line defined in this way cannot be used as a single boundary that separates the supercritical region into gaslike and liquidlike regions. For this purpose, a dynamic line on the phase diagram in the supercritical region, namely, the Frenkel line, was proposed recently [11,22–25]. The intersection of this line corresponds to radical changes of system properties. Liquids in this region exist in two qualitatively different states: rigid and nonrigid liquids. The rigid to nonrigid transition corresponds to the condition $\tau \approx \tau_0$, where τ is the liquid relaxation time and τ_0 is the minimal period of transverse quasiharmonic waves. This condition defines a different dynamic crossover line on the phase diagram and corresponds to the loss of shear stiffness of a liquid at all available frequencies and, consequently, to qualitative changes in many properties of the liquid. In contrast to the Widom line that exists only near the critical point, the present dynamic line is universal. It separates two liquid states at arbitrarily high pressure and temperature and exists in systems where the liquid-gas transition and the critical point are absent altogether. The location of the line can be rigorously and quantitatively established on the basis of the velocity autocorrelation function and mean-square displacements. It was also shown that the positive sound dispersion disappears in the vicinity of the Frenkel line [8,22–25].

In conclusion, in the present paper we proposed a van der Waals–like model that allows a purely analytical study of fluid properties including the equation of state, phase behavior, and supercritical fluctuations. We took a square-well system as an example and calculated its liquid-gas transition line and supercritical fluctuations. Employing this model allowed us to calculate the correlation length in the fluid ξ, isothermal compressibility β_T, isobaric heat capacity C_P, density fluctuations ζ_T, and thermal expansion coefficient α_T. It was shown that, in accordance with our recent results obtained for Lennard-Jones and van der Waals liquids [9,10], the bunch of extrema merges into a single line in the very close vicinity of the critical point and widens rapidly upon departure from the critical point. If the true Widom line is defined with the aid of the correlation function ξ, one can see that the Widom line does not follow the slope of any response function extrema except those located in the very close vicinity of the critical point. It seems that the Widom line defined in this way cannot be used as the boundary that separates the supercritical region into gaslike and liquidlike regions. As it has been shown recently, a different dynamic line on the phase diagram in the supercritical region, namely, the Frenkel line, can be used for this purpose [11,22–25].

As we mentioned above, the location of the lines of extrema of the different thermodynamic functions drastically depends on the trajectory in the space of the thermodynamic parameters along which we try to calculate the positions of the maxima. In the present paper we considered one of the simplest cases: We have calculated all maxima locations along the isotherms.

Here we tried to consider the simplest possible case that allows one to obtain a completely analytic description of the problem. The ideas developed in this work can be applied to other systems. It seems promising to consider the solution of the Ornstein-Zernike equation for hard spheres with a double Yukawa closure [26,27] that can model a liquid-gas transition and supercritical behavior of the system. Another possible way is to apply to the problem the effective modern technique of the solution of the nonlinear integral equations for the radial distribution function [16], which would also allow us to calculate the necessary properties.

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