Van-der-Waals supercritical fluid: Exact formulas for special lines

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In the framework of the van-der-Waals model, analytical expressions for the locus of extrema (ridges) for heat capacity, thermal expansion coefficient, compressibility, density fluctuation, and sound velocity in the supercritical region have been obtained. It was found that the ridges for different thermodynamic values virtually merge into single Widom line only at $T < 1.07T_c$, $P < 1.25P_c$, and become smeared at $T < 2T_c$, $P < 5P_c$, where $T_c$ and $P_c$ are the critical temperature and pressure. The behavior of the Batschinski lines and the pseudo-Gruneisen parameter $\gamma$ of a van-der-Waals fluid were analyzed. In the critical point, the van-der-Waals fluid has $\gamma = 8/3$, corresponding to a soft sphere particle system with exponent $n = 14$.

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A liquid-gas phase equilibrium curve onto the $T, P$ - plane ends at the critical point. At pressures and temperatures above critical ones ($P > P_c, T > T_c$), 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, where there is no difference between a liquid and a gas. An anomalous behavior of the majority of characteristics are observed in the vicinity of the critical point. The correlation length for thermodynamic fluctuations diverges at the critical point $[1]$: one can also observe a critical behavior of the compressibility coefficient $\beta_T$, thermal expansion coefficient $\alpha_P$, and heat capacity $C_v$: the given properties pass through their maxima under a change of pressure or temperature. Near the critical point, the positions of the maxima of these values in the $T, P$ - plane are close to each other $[1]$. The same is true for the value of density fluctuations, the speed of sound, thermal conductivity, etc. 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 "thermodynamical" continuation of the liquid-gas phase equilibrium curve into the supercritical region. The smearing of fluctuations, and response functions, in terms correlation length is close to a constant".

Apart from the Widom line, other "special" lines, separating a fluid state, have been suggested. The Batschinski line $[10]$, sometimes referred to as the Zeno line $[11, 12]$, corresponds to a formal coincidence between the equation of state for a fluid and the equation of state for an ideal gas.

For solids, an important thermodynamic parameter is the Gruneisen parameter which reflects the variation of the lattice dynamics under a change of density. For a fluid, one can introduce a pseudo-Gruneisen parameter $[13]$, relating such thermodynamic quantities as the heat capacity $C_v$, thermal expansion coefficient $\alpha_P$ and compressibility coefficient $\beta_T$:

$$\gamma = \alpha_P / (C_v \beta_T).$$

It is of great interest to analyze the behavior of "special" lines in a fluid and the pseudo-Gruneisen parameter in the framework of a simple, exactly solvable model. In the present study we have analyzed the properties of a van-der-Waals fluid. The van-der-Waals equation is one of the simplest equations of state for a fluid. In the reduced variables $T_r = T/T_c$, $P_r = P/P_c$, $\rho_r = \rho/\rho_c$ the equation has the form:

$$(P_r + 3\rho_r^2)(3 - \rho_r) = 8T_r \rho_r.$$
precisely ([2, 14] and refs therein). At the same time the van-der-Waals equation can be used to understand the fundamentals of fluid behavior. Besides, this equation is advantageous because exact analytical expressions can be obtained for most of the physical quantities [14]. At the same time, however strange it may look, a supercritical region of the $T, P$ - parameters for the van-der-Waals fluid model has been studied insufficiently. We know of only one study [2] analyzing the behavior of the line of the maximum of density fluctuations $\zeta_T$ in the $(\rho - T)$ (a) and $(P - T)$ (b) coordinates. The arrow indicates the approximate end of the "single" Widom line. Thick lines correspond to liquid-gas transition.

The line of the minimum of the speed of sound on the isotherms obviously corresponds to the equation (3). In [2] it was supposed that the extrema of other thermodynamic quantities in the isotherms would lie roughly on the same line. However, as we will show below, all "ridges" diverge as one goes even slightly away from the critical point.

Isothermal compressibility in the framework of the vander-Waals model has the form:

$$\beta_T = \frac{1}{\rho} \left( \frac{\partial \rho}{\partial P} \right)_T = -\frac{(\rho_r - 3)^2}{6\rho_r(-4T_r + \rho_r(\rho_r - 3)^2)}.$$ 

This line ends at its own critical point at $T_r = 1.156, P_r = 1.285, \rho_r = 0.646$ (see Fig. 1). Using a known thermodynamic relation [14], we obtain:

$$C_P - C_V = \frac{32T_r}{3(4T_r - 9\rho_r^2 + 6\rho_r^2 - \rho_r^2)}.$$ 

We remind that at $T_r > 1$ $C_V = 3/2$. It can easily be seen that the line of the maxima of the heat capacity $C_P$ in the isotherms coincides with the isochore $\rho_r = 1$ and is described in the $T, P$ coordinates by the equation:

$$T_r = \frac{3}{4} + \frac{1}{4}P_r,$$ 

i.e., represents a direct continuation of the gas-liquid equilibrium line [14] (see Fig. 1). The thermal expansion coefficient has the form:

$$\alpha_P = -\frac{1}{\rho} \left( \frac{\partial \rho}{\partial T} \right)_P = \frac{4(\rho_r - 3)}{3\rho_r(\rho_r - 3)^2 - 12T_r}.$$ 

The line of the maxima of the thermal expansion coefficient $\alpha_P$ in the isotherms corresponds to the equation

$$T_r = 3 - 2\rho(3 - \rho)^2/4.$$ 

This above line ends at zero pressure and zero density at $T_r = 27/4$ (see Fig. 1).

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 as coinciding, if the temperature values on the lines at the same pressure differ by less than 1%. The value of 1% roughly corresponds to the experimental accuracy of a measurement of the respective values and to the errors in the computer simulation data. For van-der-Waals fluid the positions of all ridges for different thermodynamic values merge into "single" Widom line in the $P, T$-coordinates at $T < 1.07T_{c}$, $P < 1.25P_{c}$ (see the inset in
FIG. 2: (Color online) Maxima of the thermal expansion coefficient $\alpha_P$, compressibility $\beta_T$, heat capacity $C_P - C_V$ in the isotherms ((a), (c), (e)) and isobars ((b), (d), (f)).

As a criterion of actual disappearance of the extremum, one can consider the ratio of a respective thermodynamic value in the maximum or minimum to this value at densities being $10\%$ different from the density in the extremum. If this ratio is below 1.01 (the difference between the extremal value and the "background" value is below $1\%$), the "ridge" can be thought of as actually smeared. When using the above criteria, the lines of all extrema, in fact, end at rather moderate temperatures and pressures: $T_r \sim 1.59, P_r \sim 2.78, \rho_r \sim 0.83$ for $\alpha_P$; $T_r \sim 1.44, P_r \sim 2.13, \rho_r \sim 0.74$ for $\zeta_T$; $T_r \sim 1.73, P_r \sim 3.9, \rho_r = 1$ for $C_P$; $T_r \sim 1.15, P_r \sim 1.35, \rho_r \sim 0.73$ for $\beta_T$; $T_r \sim 1.28, P_r \sim 1.84, \rho_r \sim 0.83$ for $V_s$ (see inset in Fig. 2(b)).

The lines of the maxima of most quantities correspond to a decrease in density with increased temperature (see Fig. 1); only the line of the maxima of the heat capacity lies on the isochore.

FIG. 3: (Color online) The Batschinski lines in the ($P - T$) (a) and ($P - r$) (b) planes. Thick lines correspond to a liquid-gas transition.

Thus, a "thermodynamic" continuation of the gas-liquid phase equilibrium line for a van-der-Waals fluid represents single Widom line if the temperature moves only $7\%$ away from the critical point; if the temperature moves further away, it represents a rapidly widening bunch of lines, which in fact ends at $T_r < 2, P_r < 5$.

Let us discuss now the Batschinski line, sometimes referred to as the Zeno line. This line corresponds to the equation $PV/RT = 1$. A.I. Batschinski demonstrated that within the van-der-Waals model, the above line will be straight in the coordinates $\rho, T$. In most studies, the behavior of this line was only analyzed in the $\rho, T$ coordinates for model and real systems. At the same time it is of interest to examine not only the behavior of this line but also the behavior of other lines determined by the condition $PV/RT = Z$ both in the $\rho, T$ and $P, T$-planes. Fig. 3 presents the lines satisfying the conditions $PV/RT = Z$ for a van-der-Waals fluid, obtained from the equation:

$$T_r = \frac{3\rho_r(3 - \rho_r)}{8 - k(3 - \rho_r)}.$$  

For the Batschinski line, we have the expression $T_r = \frac{\alpha}{8}(3 - \rho_r)$. In this case, it should be taken into ac-
count that the condition $PV/RT = Z$ in the reduced units has the form: \( \frac{\rho_r}{\rho_c} = k \), where \( k = 8/3 \) corresponds to the condition $PV/RT = 1$. The behavior of the lines if $PV/RT < 1$ and $PV/RT > 1$ is quite different. The Batschinski line, determined by the equation $PV/RT = 1$, separates two regions of a fluid: a "soft" low density fluid with the predominance of the attractive potential as compared to an ideal gas, where $PV/RT < 1$, and a more "rigid" higher density fluid with the predominance of the repulsive potential as compared to an ideal gas, where $PV/RT > 1$ (see Fig. 3). Therefore, the line $PV = RT$ can be called "separatrix". The Batschinski separatrix is the only line of the given family which ends at zero density and pressure, where it coincides with the ideal gas regime. The Batschinski separatrix for the van-der-Waals fluid ends at $T_r = 27/8$, i.e., the same temperature at which the lines of the maxima of density fluctuations and minima of the speed of sound end. This coincidence is related to the fact that these lines correspond to the zero of the second pressure derivative of the density. For an ideal gas, this derivative is equal to zero at all temperatures, so the line of the maxima of the value \( \zeta_r \) at zero density corresponds to the ideal gas equation $PV = RT$ as well.

Finally, let us analyze the behavior of a pseudo-Gruneisen parameter for a van-der-Waals fluid. Using the equation (11) we have:

$$\gamma = \frac{16}{3} \frac{\rho_r}{(3 - \rho_r)}. \quad (8)$$

For the majority of real substances, the Gruneisen parameter varies in the range from 0.5 to 3, i.e., the van-der-Waals fluid in the region of "normal" densities (2-2.5) for liquids has anomalously high Gruneisen parameter values. For a system of particles with a purely repulsive exponential interaction (soft sphere system), the Gruneisen parameter value can easily be deduced: $\gamma = (n + 2)/6$, where $n$ is the exponent of the repulsive potential. Thus, $\rho_r = 3$ limit obviously corresponds to hard sphere system ($n = \infty$). At the critical point, $\gamma = 8/3 \approx 2.67$, that is, coincides with the value for a soft sphere system with $n = 14$, which is close to the exponent in the repulsive part of Lennard-Jones potential ($n = 12$). The behavior of real rare gas substances, too, is well described by the potential of soft spheres with $n = 12 - 13$. Thus, the melting curve for argon coincides, to a high accuracy, with that for a soft sphere system with $n = 12.7$ [13, 14]. Rare gas solids and fluids also have typical values of the Gruneisen parameter $\gamma \sim 2.3 - 2.6$ [13, 14]. Thus, the van-der-Waals fluid near the critical point has the Gruneisen parameter values close to those for real rare gas fluids. In this regard, a success in the description of the properties of rare gas fluids by van-der-Waals equation in the vicinity of the critical point can better be understood.

Summing up, one can conclude that in the framework of the van-der-Waals equation it has been possible to obtain exact analytical expressions for the "special" lines in the region of a supercritical fluid and for the pseudo-Gruneisen parameter. The qualitative inferences made in the present study will obviously be valid for real simple fluids as well. This is particularly true of the conclusion about how far from the critical point we may establish a single Widom line for different thermodynamic values, and how far from the critical point the extrema of particular physical quantities can still be followed. Of course, the behavior of ridges for thermodynamic values may be different and depends on corresponding equation of state [1]. However, as for the liquid-gas transitions at enough high pressures ($P_r > 10$), it is dynamic, not thermodynamic, characteristics that should be considered when separating a fluid into liquid-like and gas-like regions.

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