

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/51074030>

Unified Picture for the Classical Laws of Batschinski and the Rectilinear Diameter for Molecular Fluids

ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY B · MAY 2011

Impact Factor: 3.3 · DOI: 10.1021/jp201872f · Source: PubMed

CITATIONS

9

READS

23

2 AUTHORS:



Leonid Bulavin

National Taras Shevchenko University of Kyiv

323 PUBLICATIONS **829** CITATIONS

SEE PROFILE



Vladimir L Kulinskii

Odessa National University

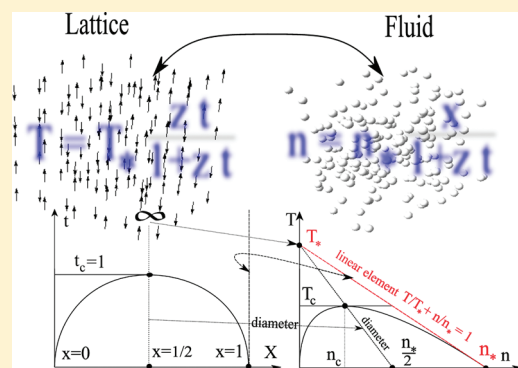
55 PUBLICATIONS **193** CITATIONS

SEE PROFILE

Unified Picture for the Classical Laws of Batschinski and the Rectilinear Diameter for Molecular Fluids

L. A. Bulavin^{*,†} and V. L. Kulinskii^{*,‡}[†]Department of Molecular Physics, Taras Shevchenko National University of Kyiv, 2 Prosp. Academician Glushkov, Kyiv 03022, Ukraine[‡]Department for Theoretical Physics, Odessa National University, Dvoryanskaya 2, 65026 Odessa, Ukraine

ABSTRACT: The explicit relations between the thermodynamic functions of the lattice gas model and the fluid within the framework of an approach proposed earlier [Kulinskii, V. L. *J. Phys. Chem. B* 2010, 114, 2852] are derived. It is shown that the Widom line serves as the natural border between the gas-like and the liquid-like states of the fluid. The explanation of the global cubic form of the binodal for the molecular liquids is proposed, and the estimate for the amplitude of the binodal opening is obtained.



■ INTRODUCTION

There are two classical laws for the molecular liquids that have been known for more than a century. For a long time, they were considered as mere curious facts restricted to the simple van der Waals equation of state (vdW EoS). The first of them is the law of the rectilinear diameter (LRD).^{1,2} It states that the diameter of the coexistence curve in terms of density–temperature is the straight line

$$\tilde{n}_d = \frac{n_l + n_g}{2n_c} = 1 + A \frac{T_c - T}{T_c} \quad A > 0 \quad (1)$$

where n_i , $i = l, g$, are the densities of the liquid and the gas phases, correspondingly, n_c is the critical density, and T is the temperature. Further, we set the Boltzmann constant to unity $k_B = 1$. Another simple linear relation is the Batschinski law³ for the vdW EoS

$$P = \frac{nT}{1 - nb} - an^2 \quad (2)$$

where P is the pressure. It states that the line determined by the condition $Z = 1$, where $Z = P/(nT)$ is the compressibility factor, is the straight line

$$\frac{n}{n^*} + \frac{T}{T^*} = 1 \quad (3)$$

Here, $n^* = 1/b$, $T^* = a/b$ is the Boyle temperature in the van der Waals approximation, and a and b are the parameters of the vdW EoS (see, e.g., ref 4). In the general case of the spherically symmetrical potential, T^* is determined in accordance with ref 5 as the following

$$T_B^{(\text{vdW})} = \frac{a}{b} \quad (4)$$

where

$$a = -2\pi \int_0^{+\infty} \Phi_{\text{attr}}(r) r^2 dr \quad (5)$$

and $\Phi_{\text{attr}}(r)$ is the attractive part of the full potential $\Phi(r)$; σ is the effective diameter of the particle, so that $b = (2\pi/3)\sigma^3$. The definition for the density parameter n^* will be given below.

The connection between two linear relations eqs 1 and 3 has attracted attention after the work of Herschbach and colleagues,^{6,7} where the line $Z = 1$ was named the Zeno line and it was shown that it is indeed almost straight for the normal fluids, though the deviations are noticeable for the accurate data. The straightness of the Zeno line implies the constraint on the contact value of the radial distribution function.⁸ Moreover, there are correlations between these linear elements and the locus of the critical point that were discovered in a series of works of Apfelbaum and Vorob'ev.^{9–11} The authors put forward the creative idea about the tangency of the Zeno line to the liquid–vapor binodal extrapolated to the nonphysical region $T \rightarrow 0$. This allowed connection to the locus of the CP with the parameters of the Zeno line

$$\frac{T}{T_B} + \frac{n}{n_B} = 1 \quad (6)$$

which are T_B and n_B . They determine the intersection points for eq 6 with the corresponding axes. According to former

Received: January 13, 2011

Revised: April 1, 2011

Published: April 25, 2011

treatments,^{6,7,9,10} T_B is the Boyle temperature, that is

$$B_2(T_B) = 0$$

and n_B is determined by the relation

$$n_B = \frac{T_B}{B_3(T_B)} \left. \frac{dB_2}{dT} \right|_{T=T_B} \quad (7)$$

where B_n is the virial coefficient of n th order.⁴

Equation 1 fails at the vicinity of the critical point (CP) where the singular terms appear^{12,13} (see also recent works^{14–16}). Nonlinear deviations from the linearities in eqs 1 and 6 in the low-temperature region, for example, for water, can be associated with the presence of the anisotropic interactions like H-bonds.¹⁷ Despite the deviations from the exactly linear behavior, eqs 1 and 3 are much more general and can be considered as the nontrivial extension of the principle of corresponding states.⁷

In ref 18, it was shown that both eqs 1 and 3 as well as the correlations between these linear elements and the locus of the critical point can be considered as the consequence of the global mapping between the liquid–vapor part of the phase diagram and that of the lattice gas (LG). The latter is described by the Hamiltonian

$$H = -J \sum_{\langle ij \rangle} q_i q_j - h \sum_i q_i \quad (8)$$

Here, q_i is the site filling number and $q_i = 0, 1$ indicates whether the site is empty or occupied, respectively. The quantity J is the energy of the site–site interaction of the nearest sites i and j , and h is the field conjugated to the filling variable q_i . We denote by t the temperature variable corresponding to the Hamiltonian eq 8. The density parameter is the probability of occupation of the lattice site $x = \langle q_i \rangle$.

If the LRD is assumed, then such mapping is given by

$$n = n^* \frac{x}{1+z} \quad T = T^* \frac{zt}{1+zt} \quad (9)$$

where z , n^* , and T^* are some parameters, which are connected with the coordinates of the CP

$$z = \frac{T_c}{T^* - T_c} \quad (10)$$

$$n_c = \frac{n^*}{2(1+z)} \quad (11)$$

$$T_c = T^* \frac{z}{1+z} \quad (12)$$

This transformation is uniquely determined by the correspondence between the characteristic linear elements on the phase diagrams of the fluid and the LG. It is assumed that the coordinates of the CP for the LG are normalized so that $t_c = 1$ and $x_c = 1/2$. In such a context, the parameter z represents the class of the corresponding states.¹⁹ Note that at $z \rightarrow 0$ and $T^* \rightarrow \infty$ with $zT^* \rightarrow 1$ from eq 9, we get $n/n^* \rightarrow x$ and $T \rightarrow t$.

The application of the transformation to the calculation of the locus of the CP of Lennard-Jones fluids is given in refs 19 and 20. The strong argument in favor of the choice of the linear element eq 3 with the parameters n^* and T^* instead of those for the Zeno line in eq 6 and the comparison of the values for various potentials are given in refs 19 and 21. There, eq 9 was used to

map the binodal of the planar Ising model onto the binodal of the two-dimensional Lennard-Jones fluid.

The aim of this paper is to discuss the physical basis of the linearities of eqs 1 and 6 on the liquid–vapor part of the phase diagram of the fluids. We will follow the results of refs 18 and 19. We expand some arguments of ref 19, which concern the corrected interpretation of the Batchinski law in a way consistent with the van der Waals approximation for the EoS. Also, we derive the relation between the thermodynamic potentials for the continuum and the lattice models of fluids.

LIQUID–VAPOR BINODAL AS THE IMAGE OF THE BINODAL OF THE LATTICE MODEL

It is easy to see that linear laws eqs 3 and 6 are fulfilled trivially in the case of the LG model or, equivalently, the Ising model. Indeed, the rectilinear diameter law for the LG is fulfilled due to the symmetry of the Hamiltonian eq 8 with respect to the line $x = 1/2$.

The analogue of the Zeno line for the LG can be defined too. In this case, it is the line $x = 1$ where the “holes” are absent. This is consistent with the basic expression for the compressibility factor⁴

$$Z = \frac{P}{nT} = 1 - \frac{2\pi n}{3T} \int r^3 \frac{\partial \Phi(r)}{\partial r} g_2(r; n, T) dr \quad (13)$$

and the definition of the Zeno line as the one where the correlations determined by the repulsive and the attractive parts of the potential compensate each other. It is clear that if $x = 1$, then the perfect configurational order takes place, and the site–site correlation function of eq 8 vanishes

$$\langle \langle q_i q_j \rangle \rangle = \langle q_i q_j \rangle - \langle q_i \rangle \langle q_j \rangle = 0$$

Thus, the line $x = 1$ plays the role of the Zeno line on the x – t phase diagram of the LG. Due to the simple structure of the LG Hamiltonian eq 8 and explicit symmetries, there are degenerate elements of the phase diagram. The critical isochore $x_c = 1/2$ coincides with the diameter. The Zeno line is the tangent to the binodal, which in this case expands up into the region $t \rightarrow 0$. Thus, there is the degeneration of these in the case of the LG. Naturally, both mentioned degenerations for the linear elements of eqs 1 and 3 of the phase diagram disappear for the real fluids. The difference of the diameter and the isochore is nothing but the asymmetry of the binodal.²² The difference between the Zeno line and the tangent to the extrapolation of the binodal into the low-temperature region $T \rightarrow 0$ takes place only for the vdW EoS and influences directly the approach of refs 10 and 23. The latter is based heavily on the constraint of the tangency to the extrapolation of the binodal. In fact, there are no physical reasons to identify such a tangent line with the Zeno line. This is possible only for the vdW EoS. Using the generalized van der Waals approach of ref 24, any EoS can be approximated by the vdW EoS with the corresponding parameters. The definition of the tangent linear element of eq 3 relies on the van der Waals approximation for the given EoS and therefore does not coincide with the Zeno line. The value of n^* is determined by the condition analogous to eq 7

$$n^* = \frac{T^*}{B_3(T^*)} \left. \frac{dB_2}{dT} \right|_{T=T^*} \quad (14)$$

This relation follows from the constraint

$$\frac{d}{dT} \left(\frac{Z(n(T), T) - 1}{n(T)} \right) = 0 \quad (15)$$

which generalizes the condition $Z = 1$ and implies the linear change of the compressibility factor with the temperature T along the linear element eq 3.

The proposed simple relation eq 9 between the LG and the fluid may be useful for construction of the empirical EoS for the real substances. Recently, the nonlinear generalization of eq 9 has been proposed in ref 25

$$n = n^* \frac{x^\gamma}{1 + zt} \quad T = T^* \frac{zt}{1 + zt} \quad (16)$$

with γ as the fitting parameter. Unfortunately, the physical meaning of the parameter γ and its connection with the interaction potential was not discussed. Moreover, from the basic thermodynamical reasonings, the extensive parameters such as the number of particles in the LG and in fluid should be proportional unless the fluctuational effects are taken into account. The last are the source of the fluctuational induced shift of the mean-field position of the critical point.²⁶ Therefore, the modification of eq 9 in order to obtain the exact position of the critical point should be based on the inclusion of the fluctuation effects and their scaling properties. In ref 19, it was shown how the relations in eq 9 augmented with some scaling considerations allow one to obtain the CPs of the Lennard-Jones fluids based on the properties of the potentials. The difference between T_B and T^* and n_B and n^* is indeed essential especially in high dimensions, $d > 3$.²⁰

In the next section, we propose the generalization of the transformation in eq 9 for the procedure of the symmetrization of the binodal of the fluid, which preserves the correspondence between the extensive thermodynamic quantities.

■ SYMMETRIZATION OF THE BINODAL

We believe that the key point which determines the form of the mapping is the LRD eq 1. The linear element eq 3 plays an auxiliary role and defines the proper scales for the density and the temperature.

As was shown earlier in ref 21, the transformation in eq 9 allows mapping of the binodal $T_{\text{bin}}(n)$ of the Lennard-Jones fluid onto the binodal $t_{\text{bin}}(x)$ of the corresponding LG model. The latter has explicitly symmetric shape with respect to the critical isochore $x_c = 1/2$

$$t_{\text{bin}}(\tilde{x}) = t_{\text{bin}}(-\tilde{x}) \quad \tilde{x} = 1/2 - x, \quad x \leq 1/2 \quad (17)$$

due to the particle–hole symmetry of the Hamiltonian eq 8. Thus, one can treat eq 9 as the procedure of the symmetrization of the phase diagram. Indeed, suppose that $n_d(T)$ is the dependence of the density diameter. Then, the variable $n/n_d(T)$ is symmetrical over the binodal. With this, eq 9 may be generalized as follows

$$x = \frac{n}{2n_d(T)} \quad T/T^* = 1 - f(t) \quad (18)$$

where the parametrization function f is chosen so as to map the binodal of the fluid $T_{\text{bin}}(n)$ onto the binodal of the LG $t_{\text{bin}}(x)$. It can be found from the common conditions of the thermodynamic

equilibrium, $P(n_g, T) = P(n_l, T)$. The equality of the chemical potentials is fulfilled due to symmetry of the binodal of the LG (see also Figure 2).

The transformation in eq 9 is the particular case for which

$$n_d(T) = \frac{n^*}{2} f(t) \quad f(t) = \frac{1}{1 + zt}$$

In the simplest linear approximation for the temperature behavior of the diameter n_d of the form in eq 1, obviously

$$n/n^* = x f(t) \quad T/T^* = 1 - f(t). \quad (19)$$

The unknown parametrization function f is determined by the condition

$$P(n_l, T) = P(n_g, T) \quad (20)$$

To illustrate this procedure, let us consider the classical vdW EoS eq 2. Using the symmetry of the LG representation in eq 19 with respect to $x_c = 1/2$, it is convenient to represent the densities of the coexisting phases as $n_g = x f(t)$ and $n_l = (1 - x) f(t)$, $0 \leq x \leq 1/2$. Substituting these relations into eq 20 where the pressure P is given by eq 2, we get a simple algebraic equation for the value f

$$1 - 2f + f^2 + f^3(x - 1)x = 0 \quad (21)$$

as a function of x . In accordance with eq 19, this provides the symmetrization of the binodal of the vdW EoS in terms of the LG variable x . The result is shown in Figure 1. The corresponding coordinates of the CP in accordance with eq 19 are

$$n_c/n^* = \frac{1}{2} f(1) = 0.352 \quad T_c/T^* = 1 - f(1) \approx 0.296$$

$$P_c/(n^* T^*) \approx 0.037 \quad (22)$$

The difference between the exact values $n_c/n^* = 1/3$, $T_c/T^* = 8/27$, and $P_c/(n^* T^*) = 1/27$ is caused by the deviation of the diameter for the vdW EoS from the linear behavior. As we see, the differences are rather small. Thus, simple parametrization in eq 19 can be applied to any EoS where the deviation from the LRD can be neglected. In this case, the symmetrization of the binodal described by the parametrization in eq 18 or 19 along with the EoS for the LG could be useful in processing the data of the simulations for the coexistence curve (CC) of the Lennard-Jones fluids, where simple approximate formula

$$n_{l,g} = n_c + A|\tau| \pm B_0|\tau|^\beta \quad \tau = \frac{T - T_c}{T_c} \quad (23)$$

is used.²⁷ Also, the proposed approach allows one to avoid ambiguity in extrapolation of the binodal into the region $T \rightarrow 0$.¹⁰

In order to visualize how the splitting of the degenerate elements mentioned above occurs, it is expedient to consider the application of the transformation to the classical EoS for the LG and the Curie–Weiss molecular field approximation (see, e.g., ref 28). This equation of state has the form

$$h(m, t) = t \operatorname{arctanh}(m) - m \quad m = 2x - 1 \quad (24)$$

(Here, we neglect the trivial difference between the m -field conjugated to variable m and the x -field conjugated to x because it is irrelevant for our consideration.) The isotherms for this model EoS are shown in Figure 2a. The linear character of the transformation in eq 9 with respect to the order parameters x and

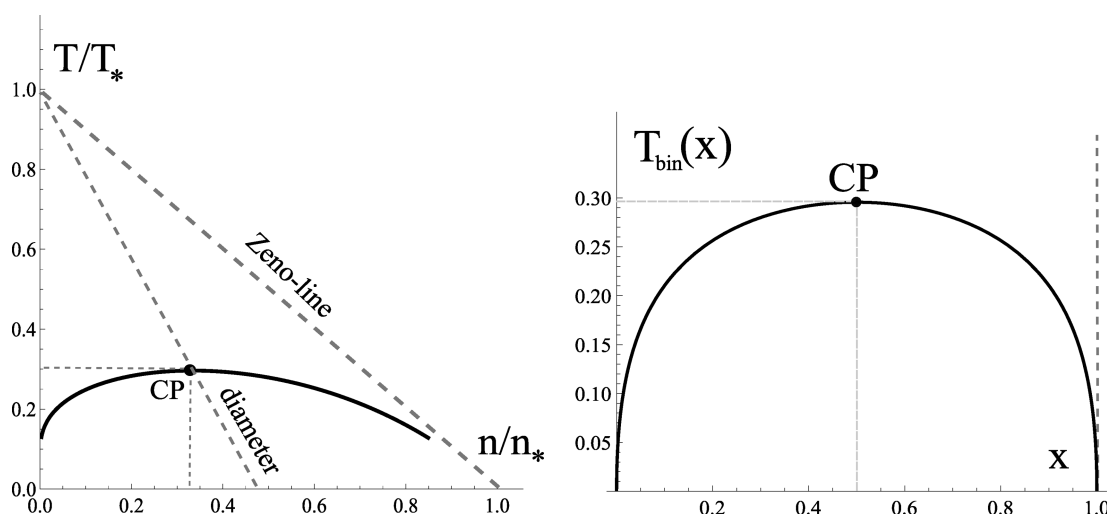


Figure 1. The symmetrization of the vdW binodal using the parametrization in eq 19 corresponding to the linear approximation for the diameter.

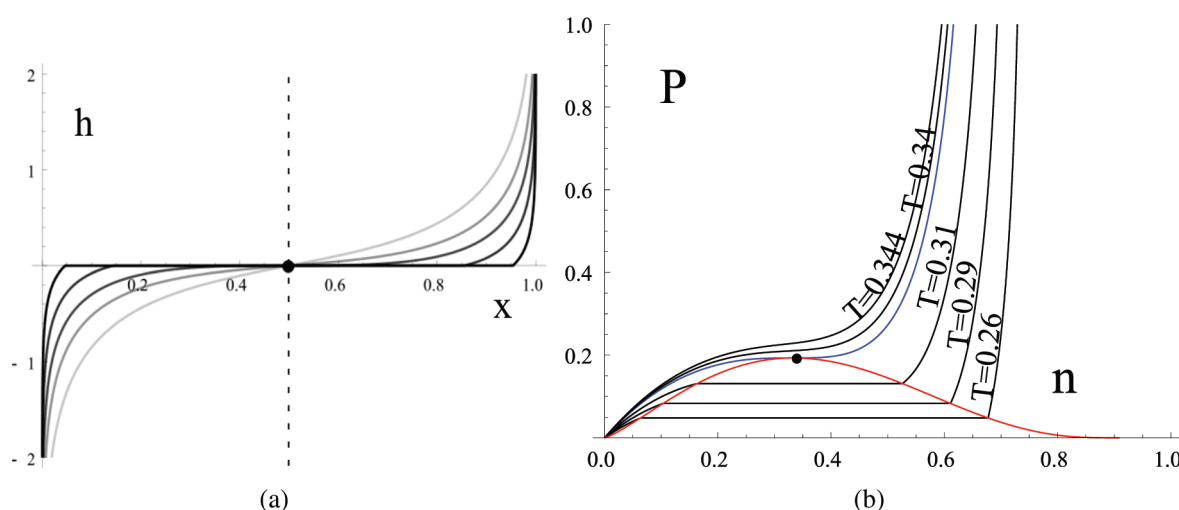


Figure 2. The isotherms obtained using eq 9 applied to the Curie–Weiss approximation for LG with $z = 1/2$. The isotherms of eq 24 are shown in (a). The corresponding isotherms for the isomorphic fluid model are in (b). The red curve is the binodal, and the critical isotherm $T_c = 1/3$ is marked by the blue line. The quantities are dimensionless (see eq 22).

n allows connection of the pressure for the asymmetrical liquid $P_{\text{liq}}(T, \mu)$ with that of the LG as follows

$$P_{\text{liq}}(T, \mu) = P_{\text{LG}}(t(T), h(\mu, T)) \quad (25)$$

The dependence $h(\mu, T)$ will be obtained in the following section (see eq 32 below). The pressure for the LG P_{LG} and, in particular, for EoS (eq 24) can be defined by the standard method (see, e.g., ref 29). Taking into account the conjugation of the thermodynamic variables, we can write

$$P_{\text{LG}}(t, h) = f(t, m) + \frac{m+1}{2}h \quad (26)$$

where $f(t, m)$ is the thermodynamic potential for the variables (t, m) . It is constructed easily using EoS eq 24, so that

$$h(t, m) = \left. \frac{\partial f}{\partial m} \right|_t \quad (27)$$

Substituting eq 26 into eq 25, we are able to construct the isotherms in the n – T plane. The result of construction of the isotherms and the binodal of the “fluid” in coordinates pressure–density based on the Curie–Weiss EoS eq 24 for the LG is shown in Figure 2.

In the following section, we discuss the relation between the thermodynamic functions of the LG and its continuum analogue in detail.

RELATION BETWEEN THE THERMODYNAMIC POTENTIALS OF THE FLUID AND THE LATTICE GAS

On the basis of the analysis of refs 21 and 25, one can expect that the transformation in eq 9 gives the relation between the phase diagram of the LG and that of the real fluid at least as the “zeroth-order approximation”. The idea that the difference between the irregularity configuration for continuum fluids and the regularity of configurations of lattice models is unimportant for consideration of the order–disorder transitions in the fluctuational region is due to K.S. Pitzer (see ref 30). However,

beyond the fluctuational region, the shape of the holes in real or continuum liquid and that in the LG causes the main difference between the configurations of these systems. From this point of view, the global character of the transformation in eq 9 shows that the particle–hole simplified picture still can be useful. Though, it is not the particle density that reflects such symmetry. Rather, the combination of the density of the particles and the density of the holes is the symmetrical variable. This rehabilitates the hole theory for expanded liquids.^{29,31} Such a caricature of the liquid state gives the possibility to relate the thermodynamic functions of these systems.

Let

$$\mathcal{G}(t, h, \mathcal{N}) = \mathcal{N} \mathcal{G}(t, h) \quad \text{and} \quad J(T, \mu, V) = P(T, \mu) V$$

be the thermodynamic potentials of the grand canonical ensembles for the LG and the fluid correspondingly. Here, \mathcal{N} is the number of sites in a lattice. First, it is natural to state the following relation $\mathcal{N} = n \cdot V$ between the extensive variables of these ensembles. The results of ref 32 allow interpretation of $1/n^*$ as the volume per particle in the ideal crystal state at $T \rightarrow 0$. Such a state defines the lattice, which may serve as the basis for the determination of the corresponding LG model.

Using the standard definitions

$$n = \frac{1}{V} \left. \frac{\partial J}{\partial \mu} \right|_T \quad \text{and} \quad x = \frac{1}{\mathcal{N}} \left. \frac{\partial \mathcal{G}}{\partial h} \right|_t \quad (28)$$

along with eq 9, we get the following relation between the potentials

$$\begin{aligned} J(\mu, T, V) &= \mathcal{G}(h(\mu, T), t(T), \mathcal{N}) \Rightarrow P(\mu, T) \\ &= n^* \mathcal{G}(h(\mu, T), t(T)) \end{aligned} \quad (29)$$

From eq 9, the relation between the density of the fluid and the density of the LG can be written as follows

$$n(\mu, T)/n^* = x(h(\mu, T), t(T))(1 - T/T^*) \quad (30)$$

Taking into account the trivial relation

$$\left. \frac{\partial}{\partial \mu} \right|_T = \left. \frac{\partial h}{\partial \mu} \right|_T \left. \frac{\partial}{\partial h} \right|_t$$

from eqs 28–30, we get the following relation

$$h(\mu, T) = (1 - T/T^*)(\mu - \mu_0(T)) \quad (31)$$

or in the inverse form

$$\mu - \mu_0(T) = h(1 + zt) \quad (32)$$

We remind the reader that $h = 0$ below CP is the coexistence line for the LG and is mapped onto the saturation curve of the continuum fluid. Therefore, $\mu_0(T)$ coincides with the chemical potential $\mu_s(T)$ along the saturation curve below the critical point $T < T_c$. To determine $\mu_0(T)$ in the supercritical region $T > T_c$, we note that the line

$$n(\mu_0(T), T)/n^* = \frac{1 - T/T^*}{2} \quad (33)$$

is the image of the line of symmetry $h = 0$ for the LG along which $x = 1/2$. Therefore, $\mu_0(T)$ defined by eq 33 can be considered as the Widom–Stillinger line of symmetry for the liquid.³³ Indeed, such line is defined as the locus of the maximum of the correlation length, where the thermodynamic response function

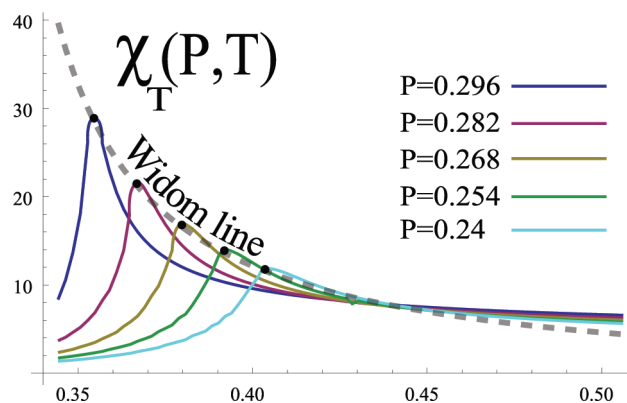


Figure 3. Widom line (dashed) as the line of the temperature maxima of the isothermal compressibility $\chi_T(P, T)$ of the fluid for different P . It is given by eq 33. The compressibility is calculated using the Curie–Weiss EoS eq 24 with subsequent transformation in eq 9.

such as the isothermal compressibility $\chi_T = 1/n(\partial n/\partial p)|_T$ has maxima $T_{\max}(P)$.³⁴ Obviously, in the case of the LG, it is represented by the line $h = 0$ or, equivalently, by the critical isochore $x = 1/2$.

The Widom–Stillinger line has attracted much attention recently in the studies on supercritical states of liquids.^{35,36} The stated mapping between the LG and the fluid naturally explains the separation of the fluid region into the gas-like and the liquid-like states with the Widom line as the border. The gas-like region is the image of the region $x < 1/2$, where the number of holes is greater than the number of particles. For the liquid-like region $x > 1/2$, the situation is inverse.

The line from eq 33 is the image of the line $h = 0$. Therefore, along this line, the continuation of the subcritical behavior (divergence) of the isothermal compressibility χ_T takes place. Figure 3 shows the result of the calculations for the compressibility χ_T in accordance with the relation in eq 29 between the fluid and the LG. This is the locus of the compressibility maxima.

From eq 29, the relation between the entropy \mathcal{S} of the LG and that of the fluid S can be derived

$$\begin{aligned} S(T, \mu, V) &= \left. \frac{\partial J}{\partial T} \right|_{\mu} = \frac{dt}{dT} \left. \frac{\partial \mathcal{G}}{\partial t} \right|_h \\ &= (1 + zt)^2 \mathcal{S}(t, h, \mathcal{N}) \end{aligned} \quad (34)$$

The results described above illustrate the general analysis of ref 13. The mapping given by eq 9 determines the fluid as the asymmetric model for the symmetric LG. The conservation of the RDL is due to the direct relation between the thermodynamic potentials in eq 29. Indeed, if a linear relation between $P(\mu, T)$ and $\mathcal{G}(h(\mu, T), t(T))$ with the analytic coefficients holds, then the quantity $(\partial P(\mu, T)/\partial h)|_T$ has the rectilinear diameter. This order parameter is the combination of the density and the entropy.^{13,15}

In order to be physically meaningful, the transformation in eq 9 or its generalization should appear as the average of the transformation of the microscopic variables. We assume that there exists such a transformation that leads to the symmetrization of the binodal. The similarity between the liquid–vapor part of the diagram for the fluid and that of the LG and also the separation between the liquid-like and gas-like states (see, e.g., ref 36)

allow one to state that for the case of fluids, there exists the “asymmetrical” microscopic observable \mathcal{A} such that

$$\langle \mathcal{A} \rangle_l + \langle \mathcal{A} \rangle_g = 0 \quad (35)$$

Here, $\langle \dots \rangle_{l,g}$ stands for the averages on the corresponding coexisting liquid and gaseous states with $(T, n_l(T))$ and $(T, n_g(T))$. In terms of ref 37, the equilibrium average $\langle \mathcal{A} \rangle_{l,g} \neq 0$ is the density-like variable, which takes different values in the coexisting phases. The specific form of the observable depends on the Hamiltonian of the fluid. Such an observable exists in the case of penetrable sphere models where the relation between the thermodynamic potentials P and \mathcal{G} is linear.¹³ In fact, the right-hand side in eq 35 can be any analytic function of T (including the neighborhood of the CP). In such a case, it is possible to redefine \mathcal{A} so that eq 35 is fulfilled. Then, the following equation

$$\langle \mathcal{A} \rangle_{\mu, T} = 0 \quad (36)$$

determines the continuation $\mu_0(T)$ of the diameter into the supercritical region $T > T_c$. Once such an observable is determined, the corresponding thermodynamic potential can be defined, so that

$$\langle \mathcal{A} \rangle = \frac{\partial \mathcal{F}}{\partial h_{\mathcal{A}}} \bigg|_S$$

In general, \mathcal{F} depends on the field variables P , μ , and T nonlinearly. Therefore, in accordance with refs 13 and 17, the density diameter shows both $1 - \alpha$ and 2β anomalies. Because the singularity of the diameter is of fluctuational nature, the transformation in eq 9 should be considered as the mean-field approximation for the transformation between microscopic fields (see ref 16).

■ CUBIC SHAPE OF THE BINODAL

The fact of the global cubic shape of the CC for the molecular liquids is the long-standing issue and was well-known to van der Waals due to studies of Verschaffelt³⁸ (see also the review³⁹). It is also a well-established fact for a wide variety of the Lennard-Jones fluids with short-ranged interactions. The results of computer simulations are well-described by the Guggenheim-like expression eq 23 (see ref 2).

The transformation in eq 9 states that the shape of the CC for the molecular fluids is determined by that for the LG.²⁰ As is known from the computer simulations,⁴⁰ the crossover to the classical behavior, which is characterized by the parabolic shape of the binodal, is absent for the LG with the nearest-neighbor interaction. On the basis of the global character of the transformation in eq 9, one can assume that the same is true for the molecular fluids with the short-ranged potentials. In other words, the binodal of the molecular fluid can be described approximately by the global cubic dependence similar to eq 23 in a broad temperature interval. In ref 21, this statement was demonstrated for 2D and 3D Lennard-Jones fluids. In particular, the binodal of the 2D Lennard-Jones fluid was obtained as the image of the binodal of the 2D Ising model given by the Onsager exact solution. In such a case, the very flat shape of the binodal dome of the 2D fluid is due to the exponent $\beta = 1/8$ and the global nature of the power-like dependence of the binodal of the 2D LG

$$x = 1/2 \pm f(t)^{1/8} \quad f(t) = 1 - \frac{1}{\sinh(2J/t)}$$

Note that $f(t)$ is the analytic function of the LG temperature variable t .

The classical Landau theory of the phase transitions gives the general picture that is characterized by the classical exponents for the critical asymptotics of the thermodynamic quantities.⁵ In particular, the dome of the binodal is given by the quadratic curve. However, it should be stressed that the Landau theory breaks the continual character of change of the thermodynamic state in passing through the CP. Indeed, there is the discontinuity of the specific heat C_V , and therefore, there is no unique critical state, but still, there are two coexisting phases. This discontinuity is connected with the assumption of the existence of the only strongly fluctuating quantity. For the liquid–vapor CP, such a quantity is the density. Indeed, if the entropy is used as the order parameter, then the finite jump of the specific heat allows one to distinguish between the ordered and the disordered phase at the CP. Besides, the parabolic shape of the binodal is the consequence of the use of the analytic EoS with application of the Maxwell construction for the pair of conjugated variables (e.g., the pressure and the volume) in the subcritical region. This puts the constraint of analyticity of the binodal in terms of the other pair of the variables, for example, the temperature and the entropy. Note that in the vicinity of the CP, $t(\tilde{x})$ should be the even function of the order parameter (see eq 17). One can expect that weak divergence of the specific heat admits the analyticity of the function $t(\tilde{x})$. Then, $t(\tilde{x}) = 1 - b\tilde{x}^{2n} + \dots$ ($b_0 > 0$), where $n > 0$ is the integer. Obviously, this occurs for $d = 2$ and ≥ 4 , where the specific heat has weak logarithmic divergence or finite jump with $n = 4$ and 1, respectively. For $d = 3$, the specific heat diverges more strongly. Therefore, one could expect that the analyticity of $t(\tilde{x})$ breaks in this case.

To clarify where the possibility for the global cubic shape of the binodal appears, let us consider the t – m phase diagram of the LG (Ising model). We use the Ising-like order parameter $m = 2x - 1$ for convenience and consider the family of the iso- h curves $t(h, m)$ for the LG. Notably, all of these curves have the inflection points $m_0(h)$. Figure 4 shows the situation for the Curie–Weiss EoS eq 24. Obviously, in the vicinity of the inflection point $m_0(h)$ determined by the condition

$$\frac{\partial^2 t(h, m)}{\partial m^2} \bigg|_{m=m_0} = 0$$

the function $t(h, m)$ has the cubic form (see Figure 4)

$$t(h, m) = t_0(h) + t_1(h)(m - m_0(h)) + \frac{t_3(h)}{6}(m - m_0(h))^3 + \dots \quad (37)$$

where the coefficients $t_1(h)$ and $t_3(h)$ are the odd functions of h . Naturally, the binodal as the line of the phase equilibrium is the curve that corresponds to $h = 0$. From this point of view, the binodal consists of two parts. They are the limiting curves of the families of cubics in eq 37 with $h > 0$ and < 0 , respectively (see Figure 4). Therefore, the binodal as the limiting curve for these families should have the cubic form

$$t(0 \pm 0, m) = 1 - \frac{t^{(0)}_3}{6} m^2 |m| + \dots \quad (38)$$

or, equivalently

$$m = B_0 |\tau|^{1/3} + \dots \quad (39)$$

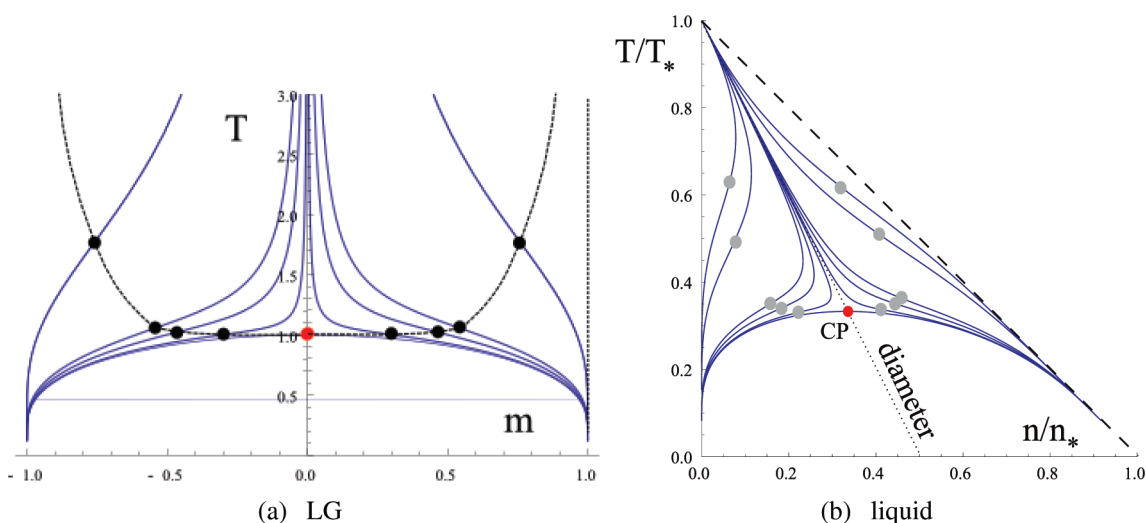


Figure 4. The phase diagram of the LG (the Ising model) and its mapping to the (n, T) plane of liquid states with the help of eq 9. The points mark the positions of the inflection points (see the text). The red point is the CP. Two families with $h > 0$ and < 0 of iso- h lines $t(h, m)$ (a) and their images in the n - T plane (b) are shown. The binodal is the limiting curve of these families.

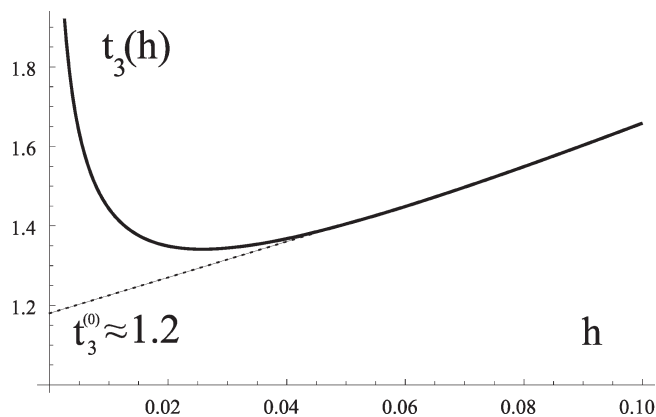


Figure 5. The behavior of the coefficient $t_3(h)$ in the Curie–Weiss approximation. The extrapolation is shown by the dashed line.

where

$$B_0 = \left(\frac{6}{t_3^{(0)}} \right)^{1/3} \quad (40)$$

In the mean-field approximation, $t_3(h) \rightarrow \infty$ in the CP. However, the analysis of the simplest Curie–Weiss approximation shows that it is reasonable to use the extrapolated value $t_3^{(0)}$ (see Figure 5). From eq 40, we obtain the value of the amplitude for the binodal opening $B_0 \approx 1.7$. Surprisingly, this coincides with the result of the corresponding value obtained in the computer simulations for the 3D Ising model.⁴¹ Under the transformation in eq 9, the iso- h lines map onto the corresponding ones in the n - T plane (see Figure 4). Obviously, the local cubic character similar to eq 37 near the inflection points takes place. Approaching the CP, we obtain the relation between the amplitudes of the LG and the continuum fluid

$$B_0^{(f)} = (1+z)^{1/3} B_0 \quad (41)$$

In accordance with the results²⁰ for the Lennard-Jones fluids, where the attractive part of the interaction has the $-1/r^6$ behavior, $z = 1/2$ in $d = 3$. Then, from eqs 40 and 41, we get

$$B_0^{(LJ)} \approx 1.95 \quad (42)$$

which is in good agreement with the value obtained in computer simulations $B_0 \approx 1.92/2.0$ for potentials of “6- n ” type.⁴²

This allows one to treat the value $\beta = 1/3$ as the corresponding exponent, which conforms with the continuity of the critical state for $d = 3$ for the systems isomorphic to the LG. Other critical indices, except the small ones α and η , which in the mean-field approximation are zeroth, can be obtained via the standard thermodynamic stability and scaling reasonings, so that $\nu = 2/3$, $\gamma = 4/3$, $\delta = 5$, and so forth.

CONCLUSIONS

In this paper, the explicit relations between the basic thermodynamic functions of the LG and the continuum fluid are derived within the global isomorphism approach proposed in ref 18. These relations allow one to obtain the information about the liquid state directly from the EoS for the lattice model. It is quite remarkable because the lattice models do not contain the translational degrees of freedom. Nevertheless, as it follows from the results,^{21,25} this mapping gives a rather good description for the LJ fluids. In particular, the stated relations can be used to connect the computer simulations for the lattice models with those for the continuum fluids (see ref 21). Within such an approach, the splitting between the critical isochore and the diameter, the Zeno line and the tangent to the binodal at $T \rightarrow 0$, is naturally described. The conservation of linear character of the diameter allows one to obtain a simple form of the transformation between the phase diagram of the LG and the continuum fluid. Obviously, the value of the critical density is the most sensitive to such an approximation. However, for the computer simulations, the deviations from the LRD are small to observe them near the CP.²⁷ This explains the rather good agreement of the estimates for the locus of the CP based on the parametrization in

eq 9 for the Lennard-Jones fluids with the results of the computer simulations.¹⁹

We believe that the approach proposed could be useful in studies of the supercritical behavior based on the EoS of the lattice models especially for water,^{34,43} where a lot of lattice models, including the models with a H-bond, are known. In view of the results of ref 36, it would be interesting to generalize the proposed approach in order to search for the correspondence between the dynamic response functions of fluids and their lattice analogues. This poses the question about the choice of the adequate lattice model of the proper geometry and the type of interaction, which realizes the isomorphism with the corresponding fluid.

AUTHOR INFORMATION

Corresponding Author

*E-mail: bulavin@univ.kiev.ua (L.A.B.); kulinskij@onu.edu.ua (V.L.K.).

ACKNOWLEDGMENT

The authors cordially thank Prof. N. Malomuzh for fruitful discussion of the obtained results and valuable comments.

REFERENCES

- (1) (a) Cailletet, L.; Mathias, E. *C.R. Hebd. séances Acad. Sci.* **1886**, 102, 1202. (b) Young, S. *Proc. Phys. Soc. London* **1900**, 17, 480–496. (c) Tsuruta, K. *Phys. Rev.* **1900**, 10, 116–122.
- (2) Guggenheim, E. A. *J. Chem. Phys.* **1945**, 13, 253–261.
- (3) Batschinski, A. *Ann. Phys.* **1906**, 324, 307–309.
- (4) Hansen, J.-P.; McDonald, I. R. *Theory of Simple Liquids*, 3rd ed.; Academic Press: New York, 2006.
- (5) Landau, L. D.; Lifshitz, E. M. *Statistical Physics (Part 1)*, 3rd ed.; Pergamon Press: Oxford, U.K., 1980.
- (6) Ben-Amotz, D.; Herschbach, D. R. *Isr. J. Chem.* **1990**, 30, 59–68.
- (7) Xu, J.; Herschbach, D. R. *J. Phys. Chem.* **1992**, 96, 2307–2312.
- (8) Song, Y.; Mason, E. A. *J. Phys. Chem.* **1992**, 96, 6852–6853.
- (9) Apfelbaum, E. M.; Vorob'ev, V. S.; Martynov, G. A. *J. Phys. Chem. A* **2004**, 108, 10381–10385.
- (10) Apfelbaum, E. M.; Vorob'ev, V. S.; Martynov, G. A. *J. Phys. Chem. B* **2006**, 110, 8474.
- (11) Apfelbaum, E. M.; Vorob'ev, V. S. *J. Chem. Phys.* **2009**, 130, 214111.
- (12) Patashinskii, A. Z.; Pokrovsky, V. L. *Fluctuation theory of critical phenomena*; Pergamon: Oxford, U.K., 1979.
- (13) Rehr, J. J.; Mermin, N. D. *Phys. Rev. A* **1973**, 8, 472–480.
- (14) Kim, Y. C.; Fisher, M. E.; Orkoulas, G. *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.* **2003**, 67, 061506.
- (15) Wang, J.; Anisimov, M. A. *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.* **2007**, 75, 051107.
- (16) Kulinskii, V.; Malomuzh, N. *Physica A* **2009**, 388, 621–627.
- (17) Reagan, M. T.; Tester, J. W. *Int. J. Thermophys.* **2001**, 22, 149–160.
- (18) Kulinskii, V. L. *J. Phys. Chem. B* **2010**, 114, 2852–2855.
- (19) Bulavin, L. A.; Kulinskii, V. L. *J. Chem. Phys.* **2010**, 133, 134101.
- (20) Kulinskii, V. L. *J. Chem. Phys.* **2010**, 133, 034121.
- (21) Kulinskii, V. L. *J. Chem. Phys.* **2010**, 133, 131102.
- (22) Sengers, J. M. L. *Ind. Eng. Chem. Fundam.* **1970**, 9, 470.
- (23) Apfelbaum, E. M.; Vorob'ev, V. S. *J. Phys. Chem. B* **2008**, 112, 13064.
- (24) (a) Rah, K.; Eu, B. C. *J. Chem. Phys.* **2001**, 115, 2634. (b) Rah, K.; Eu, B. C. *J. Phys. Chem. B* **2003**, 107, 4382–4391.
- (25) Apfelbaum, E. M.; Vorob'ev, V. S. *J. Phys. Chem. B* **2010**, 114, 9820–9826.
- (26) Ma, S. *Modern theory of critical phenomena*; W.A. Benjamin, Inc.: London, 1976.
- (27) Frenkel, D.; Smit, B. *Understanding Molecular Simulation*, 2nd ed.; From Algorithms to Applications (Computational Science Series; Academic Press, 2001; Vol. 1.
- (28) Huang, K. *Statistical Mechanics*, 2nd ed.; Wiley, 1987.
- (29) Rice, O. *Statistical Mechanics, Thermodynamic and Kinetics*; W.H. Freeman and Co.: New York, 1967.
- (30) Pitzer, K. S. *Pure Appl. Chem.* **1989**, 61, 979–988.
- (31) Barker, J. A.; Henderson, D. *Rev. Mod. Phys.* **1976**, 48, 587–671.
- (32) Apfelbaum, E. M.; Vorob'ev, V. S.; Martynov, G. A. *J. Phys. Chem. A* **2008**, 112, 6042.
- (33) (a) Widom, B.; Rowlinson, J. S. *J. Chem. Phys.* **1970**, 52, 1670–1684. (b) Widom, B.; Stillinger, F. H. *J. Chem. Phys.* **1973**, 58, 616–625.
- (34) Franzese, G.; Stanley, H. E. *J. Phys.: Condens. Matter* **2007**, 19, 205126.
- (35) Gorelli, F.; Santoro, M.; Scopigno, T.; Krisch, M.; Ruocco, G. *Phys. Rev. Lett.* **2006**, 97, 245702.
- (36) Simeoni, G. G.; Bryk, T.; Gorelli, F. A.; Krisch, M.; Ruocco, G.; Santoro, M.; Scopigno, T. *Nat. Phys.* **2010**, 6, 503–507.
- (37) Griffiths, R. B.; Wheeler, J. C. *Phys. Rev. A* **1970**, 2, 1047–1064.
- (38) Verschaffelt, J. E. *Commun. Phys. Lab. Univ. Leiden* **1896**, 2, 1–15.
- (39) Sengers, J. M. H. W. *Physica A* **1976**, 82, 319–351.
- (40) Luijten, E.; Binder, K. *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.* **1998**, 58, R4060–R4063.
- (41) Talapov, A. L.; Blote, H. W. J. *J. Phys. A* **1996**, 29, 5727–5733.
- (42) (a) Okumura, H.; Yonezawa, F. *J. Chem. Phys.* **2000**, 113, 9162–9168. (b) Camp, P. J.; Patey, G. N. *J. Chem. Phys.* **2001**, 114, 399–408. (c) Ou-Yang, W.-Z.; Lu, Z.-Y.; Shi, T.-F.; Sun, Z.-Y.; An, L.-J. *J. Chem. Phys.* **2005**, 123, 234502.
- (43) Abascal, J. L. F.; Vega, C. *J. Chem. Phys.* **2010**, 133, 234502.