Simple Geometrical Interpretation of the Linear Character for the Zeno-Line and the Rectilinear Diameter

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Received: December 16, 2009; Revised Manuscript Received: January 26, 2010

The unified geometrical interpretation of the linear character of the Zeno-line (unit compressibility line $Z = 1$) and the rectilinear diameter is proposed. We show that recent findings about the properties of the Zeno-line and striking correlation with the rectilinear diameter line as well as other empirical relations can be naturally considered as the consequences of the projective isomorphism between the real molecular fluids and the lattice gas (Ising) model.

Introduction

Searching for the similarity and the unifying principles in the description of the variety of the thermodynamical properties of complex matter is the key point of statistical physics. One of the most known is the principle (theorem) of corresponding states (PCS) which goes back to van der Waals.[1] Of course this law is approximate because of the difference in intermolecular forces for different substances. Strictly speaking the PCS is applicable only to the substances which have similar interparticle potentials.[2] Moreover the PCS is pure classical since it is based on the continuous scaling of the characteristic of the interparticle potential. The quantum effects which lead to the discrete number of the energetic levels in the potential well lead to the deviation from this law even for heavy noble gases.[3] In such a case the search of the universal relations which applicable to broad class of substances is of great importance. Well-known the rectilinear diameter law (RDL)[4] for the density as the order parameter of the phase coexistence:

$$n_{\rm d} = \frac{n_{\rm liq} + n_{\rm gas}}{2n_{\rm c}} - 1 = A|\tau| + ... \qquad \tau = \frac{T - T_{\rm c}}{T_{\rm c}} \tag{1}$$

is one of the examples. Although the relation 1 is also approximate it is observed for a wide variety of fluids in a surprisingly broad temperature interval beyond the critical region where the critical fluctuations lead to the appearance of the non analytic corrections[5] (for the recent review see[6]).

Another typical phenomenological Batchinsky law was derived from the van der Waals equation.[7] It states that the curve defined by the equation $Z = 1$, where $Z = (P)/(nT)$ is the compressibility factor, is a straight line which can be described by simple equation on (n, T) -plane:

$$\frac{n}{n_{\rm B}} + \frac{T}{T_{\rm B}} = 1 \tag{2}$$

The temperature $T_{\rm B}$ corresponds to the Boyle point[8] and $n_{\rm B}$ is the value of the density obtained by the extrapolating the coexistence curve into the low temperature region beyond triple

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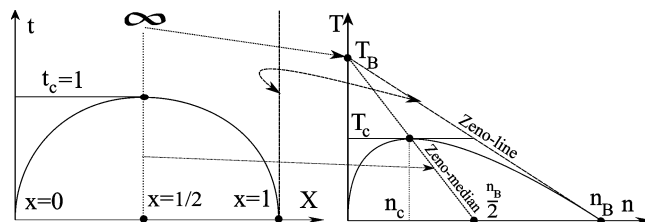
Figure 1. Geometrical correspondence between the elements of the thermodynamic phase diagram. The interaction constant is normalized $J = 1$. The Zeno-line $Z = 1$ and the Zeno-median are shown. The latter coincides with the diameter of the binodal.

point.[9] In work of Ben-Amotz and Herschbach[8] the line $Z = 1$ is called by the Zeno-line (ZL). They also noted the striking correlation between two remarkable linearities 1 and 2.

These findings have been further developed in works of Apfelbaum et al.[9−11] and successfully applied for the prediction of the critical points of high-temperature metals.[12] Two main empirical facts discovered in these works are very important. The first one is the fact that the ZL tends asymptotically to the liquid branch of binodal at low temperatures. The second fact is that the corresponding median asymptotically close to the rectilinear diameter at $T \to 0$. These facts allow to formulate the conception of the "Triangle of Liquid-Gas States".[11] The authors also claimed that the RDL can be considered as the consequence of the linear dependence of the Zeno line at low temperatures.

The aim of this work is to propose simple geometrical interpretation which naturally explains the linearities 1 and 2 as the consequence of (approximate) isomorphism of the real fluids with the lattice gas.

Linearity of the Zeno-Line and the Density Diameter

The geometrical fact that the ZL is the tangent to the coexistence curve allows us to state that there is global isomorphism between the phase diagram of the lattice gas (LG) or equivalently the Ising model and the liquid−gas part of the diagram of the simple fluid with the coexistence region extrapolated in the region $T \to 0$. The phase diagram of the LG is remarkably symmetrical (see Figure 1). This is the reflection of the particle-hole symmetry which in real fluids is absent due to finite size of the particles and the infinite repulsive potential

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at small distances.[13] In particular the specific shape of the particles influences the equation of state.[14]

The Hamiltonian of the lattice gas is:

$$H = -J \sum_{\langle ij \rangle} n_i n_j - \mu \sum_i n_i \quad (3)$$

where J is the energy of the site−site interaction of the nearest sites i and j, μ is the chemical potential. This Hamiltonian is trivially isomorphic to the Hamiltonian of the Ising model of interacting spins s_i via the transformation $n_i = (1 + s_i)/(2)$, $s_i = \pm 1$ so that $n_i = 0, 1$ whether the site is empty or occupied correspondingly. The order parameter is the probability of occupation $x = \langle n_i \rangle$ and serves as the analog of the density.

Indeed there are two specific elements which determine the structure of the liquid−gas part of the phase diagram. The first one is the coexistence line which is terminated by the second element - the critical point (CP). The comparison of the phase diagram of the LG and the real fluid shows that they are topologically isomorphic. Therefore the one-to-one correspondence between the basic elements can be given (see Figure 1). Moreover taking into account the linearities of the characteristic elements like diameter of the binodal and the Zeno-line such isomorphism can be chosen in the simplest form of the projective mapping since it conserves the incident and tangential relations between the corresponding linear elements. Moreover the transformation of such class is unique because any projective transformation is determined by the correspondence between two triplets of three nonconcurrent lines.[15] In our case we choose the following triplets the critical isotherms, the Zeno-lines and the Zeno-medians:

$$t_c = 1 \leftrightarrow T = T_c, \quad x = 1/2 \leftrightarrow \frac{2n}{n_B} + \frac{T}{T_B} = 1,$$

$$x = 1 \leftrightarrow \frac{n}{n_B} + \frac{T}{T_B} = 1 \quad (4)$$

As a sequence, the binodal of the LG is mapped onto binodal of the real fluid. Thus the projective nature is based on the fact that the ZL must be tangential to the extension of the liquid branch of the binodal in low temperature region stated in.[11]

Basing on the consideration above we can find the corresponding projective transformation between (x, t) and (n, T) planes which maps these configurations onto each other. This transformation has the following general form (see, e.g., ref 15):

$$n = \frac{ax + bt + c}{dx + et + 1} \qquad T = \frac{hx + kt + l}{dx + et + 1} \quad (5)$$

Taking into account the correspondence between the coordinate axes:

$$x = 0 \leftrightarrow n = 0 \quad \text{and} \quad t = 0 \leftrightarrow T = 0$$

We can put $c = l = h = b = 0$. Finally we can write

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

where the parameter α can be derived from the correspondence between the critical points $x_c = 1/2, t_c = 1 \leftrightarrow n = n_c, T = T_c$. Elementary algebra gives:

$$\alpha = \frac{T_c}{T_B - T_c}$$

It is easy to verify that the triples 4 maps onto each other. Obviously the value of α is determined by the interparticle potential.

Note that the Boyle temperature T_B of the real fluid corresponds to the physically unreachable state with $t = \infty$ for the lattice gas. This reflects the fact that two particles of the LG can not occupy the same site because this is the prohibited configuration (occupation number n_i is either 0 or 1). Additional argument comes from the consideration of the second virial coefficient. Indeed, T_B is determined by the balance between repulsive and attractive contributions into the second virial coefficient:[16]

$$T_B = \frac{a}{b} \quad (7)$$

where

$$a = \pi \int_\sigma^{+\infty} U(r) r^2 \, dr \qquad b = \frac{2\pi}{3} \sigma^3$$

and σ is the diameter of the hard core, $U(r)$ - the potential of the long-range attractive part of the interaction. From this consideration it is clear that for point like particles $\sigma \rightarrow 0$ and $T_B \rightarrow \infty$ in accordance with 7.

Taking into account that the lattice gas CP $x_c = 1/2, t_c = 1$ maps onto the CP of real fluid n_c, T_c from 6 it is easy to get the value of the asymptotic density n_B:

$$n_B = \frac{2n_c}{1 - \dfrac{T_c}{T_B}} \quad (8)$$

This relation is the direct consequence of the proposed isomorphism and can be verified using the experimental data. In particular it is known that for many substances the approximate relation

$$T_B \approx 3T_c \quad (9)$$

is valid. Then from 8 we get:

$$n_B \approx 3n_c \quad (10)$$

Below we show how (9) and (10) follow directly from (6) augmented by the scaling properties of the LG model. Also within such geometrical approach we can derive the linearity of the critical points line which was obtained in ref 17 by the consideration of the binodals of the liquids in reduced coordinates T/T_B, n/n_B.

Indeed different molecular fluids are described by the different scales for T and n. For the corresponding lattice gas models it

means that their parameters also scales in the same way. Basing on the structure of the LG Hamiltonian 3 we can state that the phase diagram of the LG is invariant under the scale transformation

$$t \rightarrow \lambda^2 t \qquad n_i \rightarrow \lambda^{-1} n_i \qquad (11)$$

as the LG temperature parameter t is proportional to the interaction constant J. Note that this scale symmetry correlates exactly with the Lenard-Jones (LJ) potential where the leading interaction is of van der Waals nature $V(r) \propto -\varepsilon(\sigma/r)^6$. Omitting the influence of the repulsive part we get the same result since $T_c \sim \varepsilon$ and $n_c \sim 1/\langle r \rangle_c^3$, where $\langle r \rangle_c$ is the average interparticle distance at the CP. From here it follows that $T_c n_c^2$ is invariant under the scale transformation similar to (11). Of course this is nothing but the PCS for the LJ fluids which can be easily extended to other interaction potentials which have the scale invariant properties.[2]

The spatial scale in LG is determined by the state for which $x = 1$ where the lattice of particles without the hole defects is formed. This corresponds to the asymptotic state of the infinite density $n = \infty$. In the real fluid the cavities are always present. The relations 11 together with the projective isomorphism 6 lead to the fact that the point $x = 1$, $t = -2$ of intersection of the line

$$2x + t = 0 \qquad (12)$$

with the Zeno-line $x = 1$ of the LG determines the fixed point of the scale transformation. Since the point $(1, -2)$ of (x, t)-plane maps into infinite point, then 6 becomes as the following:

$$n = n_B \frac{x}{1 + \dfrac{t}{2}} \qquad T = \frac{T_B}{2} \frac{t}{1 + \dfrac{t}{2}} \qquad (13)$$

From (13) the empirical equalities:

$$n_B = 3n_c \qquad T_B = 3T_c \qquad (14)$$

follow directly. They have been used above as the empirical facts (see (10)). Under the infinitesimal transformation of the scale (11) the locus of the lattice-gas CP shifts along the line:

$$t + 6x = 4 \qquad (15)$$

which connects the points $(1/2, 1)$ and $(1, -2)$ on the LG plane. Also, the line 15 transforms into the line of the critical points on (n, T) plane:

$$\frac{n_c}{n_B} + \frac{T_c}{T_B} = \frac{2}{3} \qquad (16)$$

This situation is shown in Figure 2. Note that (16) perfectly corresponds with the equation of the critical points line:

$$\frac{n_c/n_B}{1 - a} + \frac{T_c/T_B}{1 - a} = 1 \qquad a \approx 0.33 \qquad (17)$$
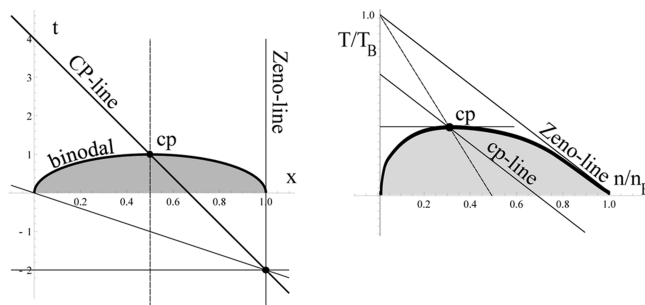

Figure 2. Zeno and CP lines for LG and real fluids.

obtained in[17] basing on the LJ model "*as the most consecutive one and the one closest to the real substances*".

So we can conclude that the fact that the value of the parameter α is close to 1/2 reflects the scale invariance property of the "r^{-6}" attractive part of the LJ potential similar to that for the LG Hamiltonian. For the real substances the parameter α depends on the repulsive part also so that $\alpha = 1/2$ is no more valid. In such a case the general form of the CP line is:

$$\frac{n_c}{n_B} + \frac{T_c}{T_B} = \frac{1 + 2\alpha}{2 + 2\alpha} \qquad (18)$$

Nevertheless, for many substances the value of α is close to 1/2 and correspondingly the estimates 14 are quite good. This allows us to give the classical Principle of Corresponding States new formulation using the proposed approach.

Discussion

We have shown that all the empirical relations about the linearity of the Zeno-line and the rectilinear diameter can casted into geometrical form. The proposed geometrical picture allows us to get the unifying view on the empirical relations obtained in refs 8−11. Such geometrical interpretation is based on the isomorphism and scaling symmetry for the Hamiltonians of the LG and the LJ fluids.

In conclusion we discuss the range of validity of the proposed isomorphism. Of course the proposed isomorphism is approximate just like the PCS. Nevertheless it provides the useful zeroth approximation for the estimates of the corresponding properties of the real substances.[12]

The range of the validity for such simple projective isomorphism is based on the conservation of the essential features of the LG. They are (a) independence of the interaction on the thermodynamical state; (b) the absence of the formation of the additional structures in liquids, e.g., polymerization, H-bond network etc. From this point of view it is expected that the linear character of both the Zeno-line and the rectilinear diameter rely on the LJ character of the interparticle interactions. This correlates with the known facts that the RDL and the linearity of the Zeno-line are violated in liquid metals metals[18] and water.[19] Also the triple point which exists in real fluids and is absent for LG leads to the deviation of the isomorphism from the simple form of the projective transformation 6. Indeed the Zeno-line is defined as the tangent to the binodal in the physical inaccessible region of $T \rightarrow 0$ and must correctly describe the low-temperature part of the binodal.[11,20] It would be interesting to elaborate the extension of the proposed approach taking into account the existence of the triple point which bounds the coexistence line at finite densities.

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The growth of the fluctuations in the vicinity of the CP is responsible for the deviation from the linearities which specified by the projective mapping. The latter is nonlinear and therefore $\langle f(n_i) \rangle \neq f(\langle n_i \rangle)$, where $\langle \cdots \rangle$ is the statistical average. In particular, in the vicinity of the CP the rectilinear diameter deviates from the simple linear law and shows anomalies.[21] Because of this the Zeno-median does not coincide with the diameter and approaches it only asymptotically far away from the CP [8,11].

Such deviations could give the support to search the isomorphism on the basis of the initial statistical local fields like in the approach proposed[22] rather than the nonlinear transformation of the thermodynamic averages only.[23]

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