Asymmetry of the Hamiltonian and the Tolman’s length

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Using the canonical transformation of the order parameter which restores the Ising symmetry of the Hamiltonian we derive the expression for the Tolman length as a sum of two terms. One of them is the term generated by the fluctuations of the order parameter the other one is due to the entropy. The leading singular behavior of the Tolman length near the critical point is analyzed. The obtained results are in correspondence with that of M.A. Anisimov, Phys. Rev. Lett., 98 035702 (2007).

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Introduction

As is known (see e.g. [1]) the Tolman length can be defined as the correction caused by the fact that the equimolar surface does not coincide with the surface of tension for a small droplet. The origin of such a difference is the asymmetry of the phase coexistence in terms of the density variable [2]. In its turn it is due to the asymmetry of the Hamiltonian. In [2] it was shown that within the square gradient model the nonzeroth value of the Tolman length is caused by the asymmetry of the density functional (Helmholtz free energy). For the symmetrical models such as lattice gas the Tolman length vanishes identically. Such a situation resembles the one with the issue of the rectilinear diameter and its singularity [3]. This effect is due to the asymmetry of the Hamiltonian as a functional of the order parameter such as density. The effects of asymmetry are consistently treated within the approach based on the canonical form of the Hamiltonian [4, 5, 6]. In such an approach both the linear [3, 7] and nonlinear [8, 9] mixing of the thermodynamic fields are treated uniformly on the basis of the isomorphism principle. In particular, the effects caused by the asymmetry of the Hamiltonian are interpreted as the sequence of improper choice of the order parameter. For proper, canonical order parameter \( \eta \) the Ising symmetry with respect to transformation \( \eta \rightarrow -\eta \) is restored. The main difference between “complete scaling” approach and the proposed approach the canonical form of the Hamiltonian lies in the fact that one does not need to use the three scaling fields but work directly with the Hamiltonian. In particular, it allows to make some conclusions about the amplitudes of the singularities.

Recently, the question about critical behavior of Tolman length is analyzed in [10] within the “complete scaling” approach. The leading singularities were obtained.

In this paper we demonstrate that the canonical formalism leads to the essentially the same results obtained in [10] in addition giving the possibility to relate the isomorphic variables with the microscopic Hamiltonian. Basing on the expressions for the Tolman length given in [2, 11] we obtain the expression for the Tolman length which explicitly demonstrates the role of the asymmetry of the Hamiltonian.

The structure of paper as follows. In Section I we give short outline of the procedure of the reduction of the Hamiltonian to the canonical form. In Section II we use the canonical transformation for structuring the Tolman length.

I. THE REDUCTION OF THE HAMILTONIAN TO THE CANONICAL FORM

We consider the case of 2-nd order phase transition. The typical examples are Ising model and simple molecular liquids. For these systems the Hamiltonian takes a form [12]:

\[
\mathcal{H}[\rho(\mathbf{r})] = H_{ql}[\rho(\mathbf{r})] + \int H_{loc}(\rho(\mathbf{r}))d\mathbf{r},
\]

where

\[
H_{loc}(\rho(\mathbf{r}); \{a_n\}) = \sum_{n=1}^{\infty} \frac{a_n}{n} \rho^n(\mathbf{r}).
\]

For convenience we include \( \beta = \frac{1}{k_B T} \) into the Hamiltonian. In a case of simple liquids, for example, the coefficients \( a_n \) are definite functions of the chemical potential \( \mu \) (in fact the difference of the chemical potential and its value \( \mu(T) \) at the coexistence curve) and the temperature \( T \) if the nontrivial reference system is used [12].
Due to locality, for every point we can write:

\[ \rho(r) = F(\eta(r)), \]

then for the integrand in the partition function of the system we have

\[ \exp\left( -H_{\text{loc}}^{\text{(can)}}(\eta) \right) = \int \delta(\rho - F(\eta)) \exp\left( -H_{\text{loc}}^{\text{(can)}}(\rho) \right) d\rho, \]

where

\[ H_{\text{loc}}^{\text{(can)}}(\eta) = A_1 \eta + \frac{A_2}{2} \eta^2 + \frac{A_4}{4} \eta^4. \]

Here we give the procedure of transforming the Hamiltonian to canonical form using the ideas of the Catastrophe Theory \[13\]. The link of the CF with the CT is the transformation \( \rho \to \eta(\rho) \) of the initial order parameter. Similar idea of transformation of the variable reducing the distribution to simpler (gaussian) form was used in \[14\].

It is expedient to represent the local part of the fluctuation Hamiltonian as the sum of even “(+)” and odd “(−)” parts:

\[ H_{\text{loc}}(\rho(r)) = \sum_{n=1}^{\infty} \frac{a_n}{n} \rho^n(r) = H_{\text{loc}}^{(+)}(\rho(r)) + H_{\text{loc}}^{(−)}(\rho(r)) \]

For the local part the Hamiltonian we can write:

\[ F[\tilde{\eta}] = G[\rho], \]

where

\[ F[\tilde{\eta}] = \int_{0}^{\tilde{\eta}} \exp\left( -H_{\text{loc}}^{\text{(can)}}(z) \right) dz \]

\[ G[\rho] = \int_{0}^{\rho} \exp\left( -H_{\text{loc}}(z) \right) dz. \]

The coefficients \( A_1 \) and \( A_2 \) of the canonical form are determined basing on the equalities

\[ F[+\infty; A_1, A_2, A_4] = G[+\infty; \mu, T] \]
\[ F[-\infty; A_1, A_2, A_4] = G[-\infty; \mu, T] \]

which provide the bijectivity of the transformation given by Eq. (7). To be specific we assumed that the coefficients of the initial Hamiltonian depend on the “laboratory” variables chemical potential \( \mu \) and the temperature \( T \). Two conditions (8) are not sufficient to fix three coefficients \( A_1, A_2, A_4 \) as functions of the “laboratory” variables. The coefficient \( A_4 \) can be fixed according to some additional condition since it is assumed that \( A_4 \neq 0 \).

Let us describe how the coefficients of the canonical form relate with the laboratory variables. Note that the Hamiltonian \( (6) \) is usually based on the mean-field equation of state. Therefore neglecting the fluctuations the coefficients of the canonical form can be found from the condition of invariance of the CP locus within the local (mean-field) approximation (the sum of even “(+)” and odd “(−)” parts):

\[ A_1(\mu_c, T_c) = 0, \quad A_2(\mu_c, T_c) = 0 \quad \Leftrightarrow \quad a_1(\mu_c, T_c) = 0, \quad a_2(\mu_c, T_c) = 0. \]

These equations fix the value of \( A_4 \):

\[ \int_{-\infty}^{+\infty} \exp\left( -\frac{A_4}{4} \eta^4 \right) d\eta = \int_{-\infty}^{+\infty} \exp\left( -H_{\text{loc}}(\rho; a_1 = 0, a_2 = 0) \right) d\rho, \]

which gives

\[ A_4^{(0)} = \frac{\pi^4}{\left( \Gamma\left( \frac{3}{4} \right) \int_{-\infty}^{+\infty} \exp\left( -H_{\text{loc}}(\rho; a_1 = 0, a_2 = 0) \right) d\rho \right)^{\frac{1}{4}}}. \]
But bearing in mind the account of fluctuations we do not need such an approximation. Moreover the fluctuations change the locus of the critical point. Taking into account the subsequent renormalization of the Hamiltonian \( H \), it is natural to put \( A_4 \) equal to the renormalized interaction constant \( u^* \) of the nongaussian fixed point:

\[
A_4 = u^* \tag{12}
\]

and use the representation \( A_2 = r^* + \tau \), where \( r^* \) is the coordinate of the nongaussian fixed point \( r^* = -\frac{\xi}{6} \Lambda^2 + o(\varepsilon) \) and \( \Lambda \) is the momentum cutoff \( [16] \). In particular the critical point is determined by:

\[
A_1(\mu_c, T_c) = 0, \quad A_2(\mu_c, T_c) = r^*,
\]

Since the transformation \( [3] \) is smooth, the coefficients \( A_i \) are the smooth functions of the laboratory variables. In particular at the coexistence curve for liquid-vapor transition we have:

\[
A_2(\mu, T)|_{A_1=0} = a \tau + o(\tau), \tag{13}
\]

\[
a > 0, \quad \tau = \frac{T - T_c}{T_c}.
\]

Thus the coefficients \( A_1 \) and \( A_2 \) of the canonical form can be treated as the scaling fields. This is the approximation, because the higher gradient terms are omitted. But since such terms do not contribute to the renormalization of the local terms we can expect that such an approximation incorporates the main thermodynamic features of the interparticle interactions. Thus in variable \( \eta \) the Hamiltonian functional takes the Landau-Ginzburg form:

\[
H_{LG}[\eta(r)] = \int \left(A_1 \eta + \frac{A_2}{2} \eta^2 + \frac{A_4}{4} \eta^4 + \frac{1}{2} (\nabla \eta)^2 \right) dV, \tag{14}
\]

where we scaled the square gradient term appropriately. Expanding Eq. \( [7] \) in a series we get:

\[
\eta(r) = \rho(r) + \frac{1}{2} \Gamma_2 \rho(r)^2 + \frac{1}{3} \Gamma_3 \rho(r)^3 + \frac{1}{4} \Gamma_4 \rho(r)^4 + \ldots,
\]

where all coefficients are functions of the “laboratory” variables (e.g. \( \mu \) and \( T \)):

\[
\Gamma_2 = a_1 + A_1, \\
\Gamma_3 = \frac{1}{2} \left( a_2 + a_1^2 + A_2 + A_1^2 + 3 a_1 A_1 \right), \\
\Gamma_4 = \frac{1}{3} a_3 + \frac{1}{2} a_1 a_2 + \frac{1}{6} a_1^3 + \frac{7}{6} A_1 A_2 + A_1^3 + \frac{3}{2} a_2 A_1 + \frac{7}{6} a_1^2 A_1 + 2 a_1 A_1^2 + a_1 A_2.
\]

The approach proposed allows to treat correctly the effects caused by the asymmetry of the Hamiltonian. Note that all information about the asymmetry caused by the odd part of the local hamiltonian \( H_{loc}^{(-)} \) is represented by the linear term of the local part of of the canonical form for the Hamiltonian with \( A_1 \neq 0 \) and is encoded also into \( A_2 \) and \( A_4 \).

The influence of asymmetry of the Hamiltonian is naturally to analyse via the representation:

\[
H_{loc}(\rho(r)) = H_{loc}^{(+)}(\rho(r)) + H_{loc}^{(-)}(\rho(r)), \tag{17}
\]

\[
H_{loc}^{(+)}(\rho(r)) = \frac{H_{loc}(\rho(r)) - H_{loc}(-\rho(r))}{2},
\]

\[
H_{loc}^{(-)}(\rho(r)) = \frac{H_{loc}(\rho(r)) + H_{loc}(-\rho(r))}{2}, \tag{19}
\]

where superscripts \((+)\) and \((-)\) stand for even and odd components of the function correspondingly. Assuming that the odd part of the Hamiltonian is “small” in comparison with the even part, from Eq. \( [8] \) we obtain:

\[
A_1 = \frac{1}{\epsilon_1} \int_0^{+\infty} H_{loc}^{(-)}(x) \exp \left( -H_{loc}^{(+)}(x) \right) dx + o \left( H_{loc}^{(-)} \right), \tag{20}
\]
where
\[ c_1 = \frac{e^{\frac{\pi^2}{8\sqrt{2}}}}{2\sqrt{A_1}} \text{erfc} \left( \frac{A_2}{2\sqrt{A_1}} \right). \tag{21} \]

Neglecting the fluctuational shift of the critical point this result shows that the main contribution to \( A_1 \) comes from \( a_2 \) (assuming that the coefficients \( a_{2n+1} \) decrease with \( n \)). In [6] it was shown that the singularity of the rectilinear diameter is shared by both \( \tau^{2\beta} \) and \( \tau^{1-\alpha} \) anomalies, which are generated by the asymmetrical part of the Hamiltonian. The result of [6] together with Eq. (20) allows to relate the amplitudes of the \( \tau^{2\beta} \) and \( \tau^{1-\alpha} \) singularities with the specificity of the interparticle interaction of the system. In particular in [6] it was shown that these amplitudes have opposite signs. This is in correspondence with the results obtained in [9, 17]. From Eq. (20) it follows that perturbatively this sign is determined by the coefficient \( a_5 \). The value \( \Gamma_2 \) can be considered as the asymmetry factor. From Eqs. (16), (21) it follows that such a factor is determined by the asymmetrical part of the Hamiltonian.

Within the same approximation the coefficient \( A_2 \) is determined implicitly as:
\[ \frac{1}{2} \sqrt{\frac{A_2}{2A_1}} e^{\frac{\pi^2}{8A_1}} K_{\frac{1}{2}} \left( \frac{A_2^2}{8A_1} \right) = \int_{0}^{+\infty} \exp \left( -H_{\text{loc}}^{(+)}(x) \right) dx \tag{22} \]

where \( K_q \) is the \( q \)-th order modified Bessel function of the 2-nd kind.

The variables \( A_1 \) and \( A_2 \) unify the description of different systems near the critical point. The relations Eqs. (20), (22) relate the coefficients of the canonical form (14) with the laboratory variables. This dependence determines the critical amplitudes for the specific system.

From Eq. (15) it follows that for the average value of the density we can write:
\[ \rho = \eta_{eq} + \eta_{\text{asym}} + \ldots \tag{23} \]

where
\[ \eta_{eq} = \langle \eta(r) \rangle = \pm|A_2|^\beta g_q \left( \frac{A_1}{A_2 |A_2|^{\beta+\gamma}} \right) + \text{Wegner corrections} \]

is the equilibrium value of the canonical order parameter, and
\[ \eta_{\text{asym}} = -\frac{1}{2} \Gamma_2 \left( \eta_{eq}^2 + s_\eta \right), \quad s_\eta = \langle \eta^2(r) \rangle - \langle \eta(r) \rangle^2 = |A_2|^{1-\alpha} \left( \frac{A_1}{|A_2|^{\beta+\gamma}} \right) + \text{regular terms}. \tag{24} \]

is the part of the order parameter generated by the asymmetry of the Hamiltonian. The representation (23) together with Eq. (24) gives the general basis for treating the asymptotical properties of the physical quantities caused by the asymmetry of the coexisting phases (e.g. liquid and vapor). In particular, Eq. (24) describes the rectilinear diameter singularity [8].

Also it leads to the corresponding representation of the dimensionless (isothermal) compressibility of the coexisting phases into symmetric and asymmetric parts:
\[ \rho^2 \chi_T = \left. \frac{\partial \mu}{\partial \rho} \right|_T = \left( \frac{\partial A_1(\mu,T)}{\partial \mu} \right|_T \frac{\partial}{\partial A_1} + \left. \frac{\partial A_2(\mu,T)}{\partial \mu} \right|_T \frac{\partial}{\partial A_2} \right) \left( \eta_{eq} + \eta_{\text{asym}} \right) + \ldots = \tilde{\chi}_{\text{sym}} + \tilde{\chi}_{\text{asym}} \tag{25} \]

analogous to that obtained in [8] (see also [10]). Despite similar ideology (the nonlinear transformation of the order parameter) the formalism of the canonical form of the Hamiltonian differs from the “complete scaling” approach within the “complete scaling” approach originally proposed in [8] to treat the singularity of the rectilinear diameter and to resolve the nature of Yang-Yang anomaly [13]. The proposed approach is based directly on the Hamiltonian. This leads to the prediction that both \( \eta_{eq}^2 \) and \( s_\eta \) contributions are generated by the asymmetry of the Hamiltonian and proportional to asymmetry factor \( \Gamma_2 \). While in “complete scaling” approach they are in fact independent because of the phenomenological nature of the hypothesis of complete scaling [8, 17]. In addition the proposed approach predicts that these two contributions have opposite signs. This seems in correspondence with the estimates found [8, 9] by processing both the experimental data and model systems.

From Eq. (25) we see that in addition to the standard \( |\tau|^{-\gamma} \) singularity which is the same for both coexisting phases we get the leading correction terms \( |\tau|^{\beta-\gamma} \) and \( |\tau|^{1-\alpha-\beta-\gamma} \) which take opposite signs in these phases at the coexistence curve due to \( \eta_{\text{asym}} \). This result coincides with that of [10]. Since such terms according to [10] determine the critical behavior of of the Tolman length we will consider the application of the canonical formalism and the representation (23) to this problem.
II. CRITICALITY OF THE TOLMAN LENGTH

According to [2] the Tolman length as the coefficient of the asymptotic correction to the surface tension of a drop of radius $R$ at $R \to \infty$ is as following:

$$\delta_\rho = \frac{\int_{-\infty}^{+\infty} z \rho'(z) \, dz}{\int_{-\infty}^{+\infty} \rho'(z) \, dz} - \frac{\int_{-\infty}^{+\infty} z \rho^2(z) \, dz}{\int_{-\infty}^{+\infty} \rho^2(z) \, dz}$$  \hspace{1cm} (26)$$

where $\rho(z)$ is the equilibrium density profile of interphase coexistence. This profile is obtained basing on the minimization square gradient functional (see e.g. [1]):

$$F[\rho(r)] = \int \left( \frac{m}{2} (\nabla \rho)^2 + f[\rho(r)] \right) \, dr.$$  \hspace{1cm} (27)$$

which in fact is the LGH. In accordance with the result of previous section we perform the local canonical transformation

$$\tilde{\rho}(r) = \eta(r) - \frac{1}{2} \Gamma_2 \eta^2(r) + \ldots,$$  \hspace{1cm} (28)$$

where $\tilde{\rho} = \rho(r)/\rho_c - 1$, which restore the symmetry of the functional (27) in canonical variable $\eta$.

Note that according to the definition, the spatial profile of the canonical order parameter $\eta_{eq}(z)$ for two phase coexistence is an odd function with respect to the interphase boundary which is defined as the "equi-$\eta$" surface:

$$\eta_{eq}(-z) = -\eta_{eq}(z),$$  \hspace{1cm} (29)$$

just like for any model with the even Landau-Ginsburg functional [2]. The approach based on the correlation functions [19] gives the same result. The second term in Eq. (23) represents the asymmetry effects [4, 6]. In particular Eqs. (23), (24) lead to the "$\tau^{2\beta}$" and "$\tau^{1-\alpha}$" anomalies of the the rectilinear diameter [6]. From Eq. (29) it follows that the phase coexistence profile of the density can be written as follows:

$$\tilde{\rho}(z) = \eta_{eq}(z) + \eta_{asym}(z) + \ldots$$

with obvious Ising like properties

$$\eta_{eq}(z) = -\eta_{eq}(-z), \quad \eta_{asym}(z) = \eta_{asym}(-z),$$  \hspace{1cm} (30)$$

because of the symmetrical form of the Hamiltonian in canonical variable $\eta$. Substituting this expression into Eq. (26) we obtain:

$$\delta_\rho = -\Gamma_2 \delta_{can} + \ldots,$$  \hspace{1cm} (31)$$

where

$$\delta_{can} = \delta_\eta + \delta_s.$$  \hspace{1cm} (32)$$

Thus the amplitude value of the Tolman length is governed by the value of $\Gamma_2$, which can be either positive or negative depending on the details of the microscopic interaction. Since $\eta_{eq} \propto |\tau|^\beta$ and $\eta_{asym} \propto |\tau|^{2\beta}$ to the leading order we can write:

$$\delta_\eta = \frac{1}{2} \left( \int_{-\infty}^{+\infty} z \, d\eta_{eq}^2(z) \right) - \frac{1}{2} \int_{-\infty}^{+\infty} \eta_{eq}^2(z) \, dz, \quad \delta_s = \frac{1}{2} \left( \int_{-\infty}^{+\infty} z \, ds(z) \right) - \frac{1}{2} \int_{-\infty}^{+\infty} \eta^2(z) \, dz$$  \hspace{1cm} (33)$$

where $\eta(z)$ and $s(z)$ are the equilibrium profiles of the canonical order parameter and the entropy correspondingly.

Further we assume that the density profile varies over the correlation length $\xi$ as the only relevant characteristic spatial scale near the critical point. Below we give the ground to such an assumption using the rigorous thermodynamic
expression for \( \delta \) obtained in [11]. Then simple scaling consideration shows that the obtained contributions to Tolman
length have the following leading singular behavior

\[
\delta_\eta \propto \tau^{\beta - \nu}, \quad \delta_s \propto \tau^{1 - \alpha - \beta - \nu}.
\]

This is exactly the result obtained in [10]. The expression (31) for the Tolman length allows to give the ground for
the approximate expression

\[
\delta \simeq - \xi \frac{\rho_d - 1}{\Delta \rho},
\]

proposed in [10] basing on the asymptotic critical behavior. Here \( \rho_d = \frac{\rho_{\text{liq}} + \rho_{\text{gas}}}{2} \) is the rectilinear diameter and \( \xi \) is the correlation length. From the point of view of Eq. (23) it is definitely right qualitatively. In order to obtain the
critical amplitudes for the behavior of the \( \delta \) we use the rigorous thermodynamic expression for the Tolman length
given earlier in [2, 20] and recently represented in “compressibility form” in [11]:

\[
\delta \approx - \sigma_\infty \left( \frac{\partial \rho}{\partial \mu_T} \right) \frac{\Delta}{\left( \Delta \rho \right)^2}.
\]

(35)

Here \( \sigma_\infty \) is the surface tension of planar interface. Substituting Eq. (23) and Eq. (25) into Eq. (35) we obtain:

\[
\delta \approx 2 \sigma_\infty \frac{\chi_{\text{asym}}}{\rho_c} \left( \frac{\Delta \rho}{\Delta \rho} \right)^2 = - \frac{\sigma_\infty}{\rho_c} \frac{\partial \chi_{\text{asym}}}{\partial \mu_T} \frac{T}{4 \eta_{\text{eq}}}. \]

(36)

So that to the leading order we have:

\[
\delta \approx \frac{\sigma_\infty}{\rho_c} \frac{\partial A_1}{\partial \mu_T} \Gamma_2 \left( \frac{\hat{\eta}_g(0)}{\hat{\eta}_e(0)} |A_2| \xi^{\beta - \gamma} + \frac{\hat{\eta}_g(0)}{\hat{\eta}_e(0)} |A_2| \xi^{1 - \beta} \right) + \ldots
\]

(37)

Both expressions for Tolman length Eq. (26) and Eq. (35) give the same asymptotic behavior provided that \( \sigma \propto \xi^{-2} \propto |A_2|^2 \nu \) thus proving the assumption that the correlation length is the characteristic scale for the spatial profile
of the density and the surface tension as the specific thermodynamic potential of the interphase surface. From Eq. (37)
it follows that the amplitude of the Tolman length is determined by the asymmetry factor \( \Gamma_2 \).

Conclusion

In present paper within the canonical approach (see [4, 5]) we show that the non zeroth value of the Tolman length is
the effect of the asymmetry of the Hamiltonian of the system in density variable. Performing the transformation to the
canonical order parameter for which symmetry of the Hamiltonian is restored we derive the invariant representation
of the Tolman length in terms of the profiles of canonical order parameter \( \eta(z) \) and canonical entropy \( s(z) \). Such
a representation allows to analyse the asymptotic behavior of the Tolman length. The leading singular terms are
generated by the two above mentioned contributions and proportional to \( \propto \tau^{\beta - \nu} \) and \( \propto \tau^{1 - \alpha - \beta - \nu} \) correspondingly.
This is in correspondence with the results of [10] obtained within the “complete scaling” approach of [8]. In fact the
qualitative representation (34) shows that the nature of the singularity of the Tolman length is determined by the
singularity of the rectilinear diameter \( \rho_d \).

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[1] J. Rowlison and B. Widom, Molecular Theory of Capillarity (Claredon Press, Oxford, 1982).
[2] M. P. A. Fisher and M. Wortis, Phys. Rev. B 29, 6252 (1984).
[3] A. Z. Patashinskii and V. L. Pokrovsky, Fluctuation theory of critical phenomena (Pergamon, Oxford, 1979).
[4] V. L. Koulimskii and N. P. Malomuzh, Cond. Matt. Phys. (Ukraine) 9, 29 (1997).
[5] V. L. Kulinskii, J. Mol. Liq. 105, 273 (2003).
[6] V. L. Kulinskii and N. P. Malomuzh, The nature of the rectilinear diameter singularity (2007), URL http://www.citebase.org/abstract?id=oai:arXiv.org:cond-mat/0703459
[7] J. F. Nicoll, Phys. Rev. A 24, 2203 (1981).
[8] Y. C. Kim, M. E. Fisher, and G. Orkoulas, Phys. Rev. E 67, 061506 (2003).
[9] Y. C. Kim and M. E. Fisher, Chem. Phys. Lett. 414, 185 (2005).
[10] M. A. Anisimov, Physical Review Letters 98, 035702 (pages 4) (2007).
[11] E. M. Blokhuis and J. Kuipers, The Journal of Chemical Physics 124, 074701 (pages 8) (2006).
[12] I. Yukhnovsky and M. Golovko, The statistical theory of classical equilibrium systems (Naukova Dumka, Kiev, 1980).
[13] V. I. Arnol’d, A. Varchenko, and S. Gusein-Zade, Singularities of the differential mappings, vol. 1 (Nauka, Moscow, 1982).
[14] D. Sornette, P. Simonetti, and J. V. Andersen, Phys. Rep. 335, 19 (2000).
[15] L. D. Landau and E. M. Lifshitz, Statistical Physics, vol. 5 (Nauka, Moscow, 1976).
[16] S. Ma, Modern theory of critical phenomena (W.A. Benjamin, Inc., London, 1976).
[17] M. A. Anisimov and J. Wang, Phys. Rev. Lett. 97, 025703 (2006).
[18] C. N. Yang and C. P. Yang, Phys. Rev. Lett. 13, 303 (1964).
[19] P. Phillips and U. Mohanty, J. Chem. Phys. 83, 6392 (1985).
[20] E. M. Blokhuis and D. Bedeaux, Mol. Phys. 80, 705 (1993).