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ASYMMETRY OF THE HAMILTONIAN AND THE SINGULAR BEHAVIOR OF THE TOLMAN LENGTH WITHIN THE CANONICAL FORMALISM APPROACH

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The connection of the asymmetry of a Hamiltonian with a critical behavior of the Tolman length is studied from the point of view of a nonlinear transformation of the order parameter. It is shown that the structure of the critical asymptotics of the Tolman length is determined by that for the asymmetric part of the isothermal compressibility. The relation to the singularity of the diameter of a binodal is proved within the canonical formalism approach. It is shown how to obtain the leading critical behavior from the exact statistical mechanics expressions for the Tolman length. The results are compared with the known results by M.A. Anisimov, Phys. Rev. Lett., ***98*** *035702 (2007).*

K e y w o r d s: Tolman length, critical point, canonical form.

1. Introduction

The Tolman length can be defined as a finite-size correction to the surface tension [1]:

$$\sigma = \sigma_\infty \left(1 - \frac{2\,\delta_T}{R} + o\,(1/R)\right). \qquad (1)$$

This is the lowest order correction in terms of the Helfrich expansion of the surface tension in curvature invariants [2].

Such correction exists, because the equimolar surface and the surface of tension do not coincide for a small droplet (see, e.g., [3]). The difference is caused by the asymmetry of the coexistence phases with respect to the particle density. The study of the Tolman correction to the surface tension is of importance because of its influence on the nucleation process [4, 5]. It could be determined from the data on the saturation pressure curve as proposed in [6] on the basis of M. Fisher's droplet model [7] or directly from the equation of state (EoS) [8]. The latter approach can be applied to the nuclear matter as well [9, 10].

From the microscopic point of view, the asymmetry effects are caused by the asymmetry of a Hamiltonian. This asymmetry is explicitly reflected in the form of a Landau–Ginzburg-type effective Hamiltonian, which is the functional of the order parameter field. It was shown in [11] that, within the square gradient model, the non-zero value of the Tolman length is caused by the asymmetry of the density functional (Helmholtz free energy). For symmetric models such as the lattice gas, the Tolman length is exactly zero [11, 12]. A similar situation occurs in the case of the diameter and its singularity [13]. The singular behavior of this quantity is also generated by the asymmetry of the Hamiltonian as a functional of the order parameter [14].

The asymmetry effects can be treated consistently either from the point of view of the global isomorphism approach [15–17] beyond the fluctuational region or with the help of the canonical formalism for a fluctuational Hamiltonian in the critical region [18–20]. In particular, the effects due to the asymmetry of the Hamiltonian are consequences of the improper choice of the order parameter. Using the properly chosen order parameter, referred to as the canonical one, one restores the Ising symmetry with respect to the transformation $\eta \to -\eta$.

Recently, the question about the asymmetry of a Hamiltonian and the critical behavior of the Tolman length was studied within M. Fisher's "complete scaling" phenomenological approach [21] in a number of papers [22, 23], where the leading singularities in the Tolman length and the compressibility were obtained.

In this paper, we consider the structure of the Tolman length using the canonical formalism. Based on the expressions for the Tolman length from [11,24], we will explicitly demonstrate the effect of the asymmetry of a Hamiltonian on the value of Tolman length.

The main difference between the "complete scaling" approach [21, 23, 25] and the canonical one is as follows. In the latter case, there is no need to use three scaling fields, because the canonical approach deals directly with the Hamiltonian. In the case of systems from the Ising model universality class, the Hamiltonian depends only on two thermodynamic fields. In particular, this allows one to draw certain conclusions about the amplitudes of singularities [20].

The paper is structured as follows. The procedure for the reduction of a Hamiltonian to the canonical form is described in Section 2. In Section 3, the canonical transformation is used to obtain the structure of the Tolman length due to the asymmetry of the Hamiltonian. In Conclusion, the main results are summarized, and some problems for the future research are outlined.

2. Reduction of the Hamiltonian to the Canonical Form

We consider the case of the second-order phase transition. Typical examples are the Ising model and simple molecular liquids. If the order parameter field $\varphi(\mathbf{r})$ is chosen, the Hamiltonian of such systems takes the form [26, 27]:

$$\mathcal{H}[\varphi(\mathbf{r})] = H_{\rm ql}[\varphi(\mathbf{r})] + \int h_{\rm loc}(\varphi(\mathbf{r}))\, d\mathbf{r}, \tag{2}$$

where

$$h_{\rm loc}(\varphi(\mathbf{r}); \{a_n\}) = \sum_{n=1}^{\infty} \frac{a_n}{n} \varphi^n(\mathbf{r}). \tag{3}$$

For the quasilocal part, the square gradient approximation is usually used:

$$H_{\rm ql}[\varphi(\mathbf{r})] = \frac{b}{2} \int\limits_v dV\, (\nabla\varphi(\mathbf{r}))^2. \tag{4}$$

For the sake of convenience, we include the multiplier $\beta = \frac{1}{k_{\rm B}T}$ into the Hamiltonian. We consider also the volume V as a dimensionless quantity, because the system always has some cut-off at small distances, e.g., the size of a particle. In the case of simple liquids, if the nontrivial reference system is used, the coefficients a_n, $n \geq 1$, are definite functions of the chemical potential μ and the temperature T [26, 27]. The Ising model without external magnetic field possesses the symmetry $\mathcal{H}[\varphi(\mathbf{r})] = \mathcal{H}[-\varphi(\mathbf{r})]$, so that $a_{2n+1} = 0$ $n \geq 1$. The coefficients a_n can be calculated, in principle, with the use of the mean-field model equation of state for the reference system [23, 27, 28]. Such equations of state usually lead to a typical double-well profile for the thermodynamic potential. The two wells represent two coexistent phases, which merge at the critical point (CP) [29]. Possible transformations of the minima of the functions are the subject of study in the Catastrophe Theory (CT) (see, e.g., [30, 31]). For the case of a finite number of variables, all the possible canonical forms are classified [32]. As a matter of fact, the CT provides the mathematical basis for Landau's original idea of using a truncated φ^4-expression for the thermodynamic potential in a vicinity of the CP [29].

The main difference of our approach from the above-mentioned CT applications is in that it is based directly on the Hamiltonian rather than the thermodynamic potential. In statistical mechanics, the Hamiltonian plays a twofold role. Besides being a function on the phase space, whose average determines the internal energy, it also defines the Gibbsian probability distribution. Under the change of the variables, the density distribution function and the function itself behave differently, because of the Jacobian of the transformation appears in the former case. Using this fact, we can take advantage of freedom to choose the variables in the Hamiltonian to simplify the form of the distribution. Actually, this result is based upon the Radon–Nikodim theorem from the measure theory [33]. It states that two probabilistic measures, which has the same null-sets, can be mapped onto each other by some transformation. A similar idea of the change of variables transforming the distribution to a simpler (Gaussian) form was used in a quite different context in [34].

We search for a local transformation of the type:

$$\varphi(\mathbf{r}) = T(\eta(\mathbf{r})), \tag{5}$$

so that the η-"Hamiltonian" determining the corresponding probability density for the η-configurations takes the form of the Landau–Ginzburg Hamiltonian (LGH):

$$H_{\rm loc}^{\rm (can)}(\eta) = \int\limits_V h_{\rm loc}^{\rm (can)} dV, \tag{6}$$

$$h_{\rm loc}^{\rm (can)} = A_1\eta(\mathbf{r}) + \frac{A_2}{2}\eta(\mathbf{r})^2 + \frac{A_4}{4}\eta(\mathbf{r})^4.$$

Since the value of probability is invariant with respect to the change of the variables, the condition

$$\int\limits_{-\infty}^{+\infty} e^{-h_{\rm loc}^{\rm (can)}(x)}dx = \int\limits_{-\infty}^{+\infty} e^{-h_{\rm loc}(y)}dy \tag{7}$$

is imposed, which can be treated as the invariance of the partition function for the local part of the Hamiltonian. Equation (7) represents one of the constraints for the determination of the coefficients A_i of the canonical form as functions of the initial thermodynamic variables. It also assures the bijectivity of the transformation (5).

Let us define the functions:

$$F(\eta; A_1, A_2, A_4) = \int\limits_{-\infty}^{\eta} \exp\left(-h_{\rm loc}^{\rm (can)}(x)\right) dx, \tag{8}$$

$$G(\varphi; \{a_i\}) = \int\limits_{-\infty}^{\varphi} \exp\left(-h_{\rm loc}(y)\right) dy. \tag{9}$$

These functions are monotonic and, therefore, invertible. The desired transformation is determined correctly via the equation:

$$F(\eta; A_1, A_2, A_4) = G(\varphi; \{a_i\}), \tag{10}$$

so that the local transformation (5) is as follows:

$$\varphi(\mathbf{r}) = (G^{-1} \circ F)(\eta(\mathbf{r})), \tag{11}$$

where G^{-1} is the inverse function for G.

As has been noted before, the local part of Hamiltonian (3) is usually based on the mean-field equation of state. Therefore, by neglecting the fluctuations, i.e. considering only the local part of the Hamiltonian, we can find the coefficients of the canonical form A_i from the invariance condition for the mean-field phase diagram. Namely, the locus of the binodal $f(a_1, a_2) = 0$ and the CP are invariant with respect to the transformation of the order parameter field (5). In the canonical coordinates, the former is determined by the equation $A_1 = 0$ and the latter by $A_1 = 0$, $A_2 = 0$:

$$f(a_1, a_2) = 0 \;\Leftrightarrow\; A_1 = 0, \tag{12}$$

$$a_1(\mu_c, T_c) = 0,\; a_2(\mu_c, T_c) = 0 \;\Leftrightarrow\; A_1 = 0,\; A_2 = 0. \tag{13}$$

Of course, (7) should be consistent with this invariance condition. Therefore, from (13), we get the value of A_4:

$$\int\limits_{-\infty}^{+\infty} \exp\left(-\frac{A_4}{4}\eta^4\right) d\eta = \int\limits_{-\infty}^{+\infty} \exp\left(-h_{\rm loc}(\varphi; a_1 = 0, a_2 = 0)\right) d\varphi, \tag{14}$$

which gives

$$A_4 = \frac{\pi^4}{\left(\Gamma\left(\frac{3}{4}\right) \int\limits_{-\infty}^{+\infty} \exp\left(-h_{\rm loc}(\varphi; a_1 = 0, a_2 = 0)\right) d\varphi\right)^4}. \tag{15}$$

Equation (12) allows us to find the coefficient A_2 implicitly:

$$\sqrt{\frac{A_2}{A_4}}\; e^{\frac{A_2^2}{2A_4}}\; K_{1/4}\left(\frac{A_2^2}{2A_4}\right) = \int\limits_{-\infty}^{+\infty} \exp\left(-H_{\rm loc}(\varphi)\right) d\varphi \Big|_{f(a_1,a_2)=0}. \tag{16}$$

where K_q is the q-th order modified Bessel function of the second kind. Note that, according to (16), A_2 can be considered as a function of the temperature alone. This is because we make use the invariance of the mean-field phase diagram for the determination of the coefficients A_i. Finally, (7) determines the coefficient A_1, which depends, in general, on both thermodynamic fields.

Thus, in terms of the variable η, the Hamiltonian takes the Landau–Ginzburg form:

$$H_{\rm LG}[\eta(\mathbf{r})] = \int \left(A_1\eta(\mathbf{r}) + \frac{A_2}{2}\eta(\mathbf{r})^2 + \frac{A_4}{4}\eta(\mathbf{r})^4 + \frac{b}{2}(\nabla\eta)^2\right) dV. \tag{17}$$

The above procedure relates the coefficients A_i to the thermodynamical parameters of the system. Note that this procedure needs no small parameter and

is nonperturbative in itself due to the global nature of the Radon–Nikodim theorem. In contrast to it, the reduction of a function to the canonical form in the CT is possible only in a vicinity of the singular point. Nevertheless, the perturbative form of transformation (5) is also possible to be obtained. This can be done correctly, at least asymptotically, if one assumes that the interactions higher than φ^4 are small [35]:

$$a_n/a_4 < 1 \quad \text{for} \quad \text{n} \geq 5. \tag{18}$$

Then transformation (5) is close to the identity mapping. Expanding (11) in a series, we get:

$$\eta(\mathbf{r}) = \varphi(\mathbf{r}) + \frac{1}{2}\Gamma_2\,\varphi(\mathbf{r})^2 + \\ + \frac{1}{3}\Gamma_3\,\varphi(\mathbf{r})^3 + \frac{1}{4}\Gamma_4\,\varphi(\mathbf{r})^4 + ..., \tag{19}$$

where

$$\Gamma_2 = a_1 + A_1, \tag{20}$$

$$\Gamma_3 = \frac{1}{2}\left(a_2 + {a_1}^2 + A_2 + A_1^2 + 3a_1A_1\right), \quad etc. \tag{21}$$

Our approach allows us to treat the effects of the asymmetry of the Hamiltonian. It is natural to analyze the influence of the asymmetry of the Hamiltonian via the representation:

$$h_{\text{loc}}(\varphi(\mathbf{r})) = h_{\text{loc}}^{(+)}(\varphi(\mathbf{r})) + h_{\text{loc}}^{(-)}(\varphi(\mathbf{r})), \tag{22}$$

where

$$h_{\text{loc}}^{(+)}(\varphi(\mathbf{r})) = \frac{h_{\text{loc}}(\varphi(\mathbf{r})) - h_{\text{loc}}(-\varphi(\mathbf{r}))}{2},$$

$$h_{\text{loc}}^{(-)}(\varphi(\mathbf{r})) = \frac{h_{\text{loc}}(\varphi(\mathbf{r})) + h_{\text{loc}}(-\varphi(\mathbf{r}))}{2},$$

and the superscript $\pm$ stands for the even and odd components of the Hamiltonian, correspondingly. The calculation of the canonical coefficients for the specific case of the van der Waals equation of state can be found in [20].

Note that all information about the asymmetry caused by the odd part of the local Hamiltonian $h_{\text{loc}}^{(-)}$ is represented by the linear term of the canonical form with $A_1 \neq 0$. It is also present implicitly in A_2 and A_4. The specific calculations of the coefficients A_i for the van der Waals equation of state are presented in [20]. It follows from (10) that if the initial Hamiltonian $H_{\text{loc}}(\varphi)$ is invariant under the transformation $\varphi \to -\varphi$, then A_1 vanishes identically. This means that the canonical transformation preserves the parity of the local Hamiltonian.

Assuming that the odd part of the Hamiltonian is "small" in comparison with the even part (in the sense of (18)), relation (7) yields

$$A_1 = \left(\frac{1}{c_1}\int\limits_0^{+\infty}\left(h_{\text{loc}}^{(-)}(x)\right)^2 \exp\left(-h_{\text{loc}}^{(+)}(x)\right)dx\right)^{1/2} + \\ + o\left(h_{\text{loc}}^{(-)}\right), \tag{23}$$

where

$$c_1 = \left\{\sqrt{A_4}\Gamma\left(\frac{3}{4}\right){}_1F_1\left(\frac{3}{4};\frac{1}{2};\frac{A_2^2}{4A_4}\right) - \right. \\ \left. - A_2\Gamma\left(\frac{5}{4}\right){}_1F_1\left(\frac{5}{4};\frac{3}{2};\frac{A_2^2}{4A_4}\right)\right\}/\sqrt{2}A_4^{5/4}, \tag{24}$$

and ${}_1F_1$ is the Kummer function [36]. If we neglect the fluctuational shift of the CP, then we see that the main contribution to A_1 in a vicinity of the critical point is made by a_5 (provided the coefficients a_{2n+1} decrease, as n increases). Indeed, at the CP, $a_1 = 0$, $a_2 = 0$, $a_3 = 0$, and the first nonvanishing term in $H_{\text{loc}}^{(-)}$ is $\frac{a_5}{5}\varphi^5$.

The procedure of determination of the coefficients A_i proposed above is based on the mean field approach. The condition of invariance of the locus of the CP (13) ignores the influence of fluctuations. The fluctuations are described by the quasilocal part of the Hamiltonian, and their account shifts the locus of the CP from its mean-field position. Since the quasilocal part of the Hamiltonian has also asymmetric terms in general, the procedure of the canonical transformation should be constructed in such a way that these asymmetric terms be cancelled in the canonical Hamiltonian. The coefficients A_1, A_2, A_4 are correspondingly modified, which leads to a shift of the mean-field CP.

The appearance of such shift is connected with the inclusion of the quasilocal interaction between modes of the order parameter. It is necessary to emphasize that this shift arises before the renormalization procedure. Note that the local transformation (19) generates also the quasilocal term $\eta(\nabla\eta)^2$ multiplied by the coefficient, which is proportional to Γ_2. In this case,

all local odd power terms, as well as the term $\eta(\nabla\eta)^2$, can be cancelled. The parameter of asymmetry Γ_2 is determined by both local and quasilocal parts, which are represented in the perturbative approach by the terms φ^5 and $\varphi\left(\nabla\varphi\right)^2$, respectively. This result is in accordance with that of [14, 37], where the $\tau^{1-\alpha}$ anomaly was derived, by using the asymmetric LGH with the inclusion of irrelevant asymmetric terms of the lowest dimension, namely φ^5 and $\varphi\left(\nabla\varphi\right)^2$. There was shown that the results of the renormgroup analysis of these terms can be interpreted as a nonlinear transformation of the order parameter (see Appendix C in [14]).

It was shown in [18, 20] that the singularity of the diameter is governed by both $\tau^{2\beta}$ and $\tau^{1-\alpha}$ anomalies. The results of [20], together with Eqs. (15), (16), and (23), allow us to relate the amplitudes of the $\tau^{2\beta}$ and $\tau^{1-\alpha}$ singularities to the details of the interparticle interaction in the system. In particular, it was shown in [20] that these amplitudes have opposite signs. This fact agrees with the results obtained in [25, 38] (see also [39]) by processing the experimental data. It follows from (23) that, within perturbation theory, this sign is determined by the coefficient a_5. The value of Γ_2 can be considered as the asymmetry factor of the microscopic Hamiltonian, since it is determined by its odd part, as it follows from (20) and (23).

Applying (19), the average value of density as the initial order parameter can be written as

$$n = \eta_0 + \eta_{a\mathrm{sym}} + \dots . \tag{25}$$

where we omitted the terms of higher order which are less singular than $|A_2|^{1-\alpha}$ (see below). From this point, we restrict our consideration by the first two terms only.

Here,

$$\eta_0 = \langle\eta(\mathbf{r})\rangle = \pm|A_2|^{\beta} g_\eta\left(\frac{A_1}{|A_2|^{\beta+\gamma}}\right) + \dots$$

is the equilibrium value of canonical order parameter, and the function $g_\eta(x)$ is its scaling function [13]. The asymmetric contribution to the order parameter is

$$\eta_{a\mathrm{sym}} = -\frac{1}{2}\Gamma_2\left(\eta_0^2 + s_\eta\right), \tag{26}$$

where the quantity

$$s_\eta = \left\langle\eta^2(\mathbf{r})\right\rangle - \langle\eta(\mathbf{r})\rangle^2 = |A_2|^{1-\alpha} l_\eta\left(\frac{A_1}{|A_2|^{\beta+\gamma}}\right) + \dots \tag{27}$$

can be treated as the canonical entropy, since it is conjugated to the temperature-like variable A_2 (see (17)). The function $l_\eta(x)$ determines the critical behavior of the fluctuational part of the free energy and is connected with $g_\eta(x)$ via relation $g''_\eta(x) = l_\eta(x)$.

Representations (25) and (26) form the basis for treating the asymptotic properties of the physical quantities due to the asymmetry of the Hamiltonian. In particular, relation (26) describes the diameter singularity [20]. To compare our results with those of the complete scaling approach [21, 22]), we represent the dimensionless isothermal compressibility of the coexisting phases in a form

$$n^2\chi_T = \left.\frac{\partial n}{\partial\mu}\right|_T = \tilde{\chi}_0 + \tilde{\chi}_{a\mathrm{sym}} =$$
$$= \left(\left.\frac{\partial A_1}{\partial\mu}\right|_T \frac{\partial}{\partial A_1} + \left.\frac{\partial A_2}{\partial\mu}\right|_T \frac{\partial}{\partial A_2}\right)(\eta_0 + \eta_{a\mathrm{sym}}) + \dots, \tag{28}$$

where dots stand for the terms of the lower order as in (25). Therefore, in a vicinity if the critical point, we have

$$\chi_{\mathrm{sym}} = \frac{1}{n^2}\left.\frac{\partial A_1(\mu,T)}{\partial\mu}\right|_T |A_2|^{-\gamma} g'_s(0) + \dots, \tag{29}$$

$$\chi_{a\mathrm{sym}} = \mp\frac{\tilde{\Gamma}_2}{2n_c^2}\left.\frac{\partial A_1(\mu,T)}{\partial\mu}\right|_T \left(|\tilde{\tau}|^{\beta-\gamma} g_s(0) g'_s(0) + \right.$$
$$\left. + |\tilde{\tau}|^{\beta-1} l'_s(0)\right). \tag{30}$$

Despite the similarity in the ideology (the nonlinear transformation of the order parameter), the formalism of the canonical form of the Hamiltonian differs from the "complete scaling" approach [21], which was originally used to treat the singularity of the diameter and to resolve the nature of the Yang-Yang anomaly [40]. Note that the canonical formalism deals directly with the Hamiltonian. This leads to the prediction that both η_0^2 and s_η contributions are generated by the asymmetry of the Hamiltonian and are proportional to its asymmetry factor Γ_2. Within the "complete scaling" approach, they are actually independent, because of the phenomenological nature of the hypothesis of the complete scaling [21, 25]. In addition, our approach predicts that these two contributions are of opposite signs. This seems to agree with the estimates in [21, 38]. The analysis of [23] carried out for a number of real and model systems also reveals this fact, though some exceptions like water and

a restricted primitive model of electrolytes (see, e.g., [41]) exist. It is not clear, where this exception has really physical basis or just due to inaccuracies of the experimental data. Note that one should differentiate between the pure algebraic term $|\tau|^{2\beta}$, which can be excluded by a redefinition of the order parameter and the nonlinear fluctuational contribution to the rectilinear diameter [20, 42].

From Eq. (28), we see that, besides the standard $|\tau|^{-\gamma}$ singularity, which is the same for both coexisting phases, there are also the leading correction terms $|\tau|^{\beta-\gamma}$ and $|\tau|^{1-\alpha-\beta-\gamma}$. In these phases, they have opposite signs along the coexistence curve due to the presence of $\eta_{a\mathrm{sym}}$. This result agrees with that of [22].

Since the Tolman length is expressed via the compressibilities of the coexistent phases (see [43, 44]), the representation (28) determines the critical behavior of the Tolman length. We consider the application of the canonical formalism and representation (25) to this problem in the following Section.

3. Tolman Length and its Criticality

The question of the critical behavior of the Tolman length has been the subject of interest due to controversial conclusions made within different approaches, see [24]. The relation of the Tolman length to the asymmetry of the coexisting phases was noted by many authors [11, 12, 22].

To obtain the critical asymptotics for δ, we use the rigorous thermodynamic expression for the Tolman length derived earlier in [11, 45] and recently represented in the "compressibility form" in [24]:

$$\delta_T \approx -\sigma_\infty \frac{\Delta\left(\frac{\partial n}{\partial \mu}\Big|_T\right)}{(\Delta n)^2}. \tag{31}$$

Here, σ_∞ is the surface tension of the planar interface. Substituting Eq. (25) and Eq. (28) into Eq. (31), we obtain

$$\delta_T \approx 2\frac{\sigma_\infty}{n_c}\frac{\tilde{\chi}_{a\mathrm{sym}}}{(\Delta\tilde{n})^2} = -\frac{\sigma_\infty}{n_c}\frac{\frac{\partial \eta_{a\mathrm{sym}}}{\partial \mu}\Big|_T}{4\eta_0^2}. \tag{32}$$

So, in the leading order, we have

$$\delta_T \approx \frac{\sigma_\infty}{n_c}\left.\frac{\partial A_1}{\partial \mu}\right|_T \Gamma_2\left(\frac{g'_\eta(0)}{g_\eta(0)}|A_2|^{-\beta-\gamma} + \right.$$
$$\left. + \frac{l'_\eta(0)}{g^2_\eta(0)}|A_2|^{-1-\beta}\right) + ..., \tag{33}$$

which obviously leads to both $|\tau|^{\beta-\gamma}$ and $|\tau|^{1-\alpha-\beta-\gamma}$ singularities for the Tolman length.

Let us demonstrate how (33) can be derived directly from the basic expressions of statistical mechanics for the surface tension [46],

$$\sigma_0 = \frac{1}{4}\int dz_1 \int d\mathbf{r}_{12} u'(r) r(1-3s^2) n_2(z_1, z_2, r), \tag{34}$$

and the Tolman length, [47]:

$$\delta_T = -\frac{1}{8\sigma_\infty}\int dz_1 \int d\mathbf{r}_{12} u'(r) r(1-3s^2) \times$$
$$\times (z_1 + z_2) n_2(z_1, z_2, r), \tag{35}$$

where

$$n_2(z_1, z_2, r) = n_1(z_1) n_1(z_2)(1 + g_2(z_1, z_2, r)),$$

g_2 is the pair correlation function [48], and $n_1(z)$ is the density profile for the flat surface. There exist expressions equivalent to (34) and (35), which use the direct correlation function C_2 instead of g_2. For the surface tension, this is the Trietzenberg–Zwanzig expression [49]:

$$\sigma_\infty = T\iint dn(z_1) dn(z_2) K_2(z_1, z_2), \tag{36}$$

where

$$K_2(z_1, z_2) = \frac{1}{4}\int d^{d-1}\boldsymbol{\rho}\rho^2 C_2(z_1, z_2; \rho), \tag{37}$$

$\boldsymbol{\rho} = (x, y)$, and C_2 is the direct correlation function for the planar geometry. The expression for δ_T in the sense of the Trietzenberg–Zwanzig form was obtained by E. Blokhuis [50]. We use the result for the *cylindrical* geometry of the interface:

$$\delta_T = \frac{T}{\sigma_0}\iint dn_1(z_1) dn_1(z_2) z_1 K_2(z_1, z_2); \tag{38}$$

but, of course, the asymptotics itself does not depend on the specific geometry. Near the critical point, the density profile can be represented as follows:

$$n_1(z) = n_0 - \frac{\Delta n}{2} f(z/\xi), \quad n_0 = \frac{1}{2}(n_l + n_g), \tag{39}$$

where $\Delta n = n_l - n_g$ with $\Delta n \sim \tau^\beta$, and

$$f(z) \to \begin{cases} +1, & z \to +\infty, \\ -1, & z \to -\infty. \end{cases}$$

Note that the main contribution to the criticality of the surface tension in (38) is due to the symmetric part of the function C_2, which can be obtained on the basis of its isotropic part for the homogeneous phase. Using the standard relation

$$\frac{1}{T}\left(\frac{\partial p}{\partial n}\right)_T = 1 - n\int C_2(n;\mathbf{r}_{12})d\mathbf{r}_{12}, \tag{40}$$

along with critical asymptotics $\frac{\partial p}{\partial n}\Big|_T \propto |\tau|^\gamma$, we get

$$C_2(n;\mathbf{r}_{12}) \propto |\tau|^{2-\alpha+\gamma} \propto \frac{1}{\xi^{d+2-\eta}}. \tag{41}$$

Therefore, in the leading order, K_2 scales as

$$K_2 = \frac{1}{4}\int d^{d-1}\boldsymbol{\rho}\rho^2 C_2\left(z_1, z_2; \rho\right) \propto \frac{\xi^{d+1}}{\xi^{d+2-\eta}} \propto \frac{1}{\xi^{1-\eta}}. \tag{42}$$

Substituting this result into (36), we get the standard result for σ_0:

$$\sigma_0 \propto \frac{\Delta n^2}{\xi^{1-\eta}} \propto |\tau|^{2\beta+\nu(1-\eta)} = |\tau|^{(d-1)\nu}. \tag{43}$$

Note that the square gradient van der Waals approximation

$$\sigma_{\mathrm{vdW}} = \frac{b}{2}\int\limits_{-\infty}^{+\infty}\left(\nabla n(z)\right)^2 dz \tag{44}$$

with $b = \mathrm{const}$, which follows from (36) in the local approximation for the kernel, leads to the inaccurate critical asymptotics $\sigma_{\mathrm{vdW}} \propto |\tau|^{2\beta-\nu}$.

Similarly considering the asymmetric corrections in (40), which come from (28), we can find the critical behavior for δ_T from (38). Indeed, the inner integral expression in (37) can be decomposed into odd and even parts:

$$\mathcal{K}_1(z_1) = \int dn_1(z_2)K_2(z_1, z_2) =$$
$$= \mathcal{K}_1^{(+)}(z_1) + \mathcal{K}_1^{(-)}(z_1) \tag{45}$$

with $\mathcal{K}_1^{(\pm)}(-z) = \pm\mathcal{K}_1^{(\pm)}(z)$. Therefore, (36) and (38) are transformed into

$$\sigma_0 = T\int dn_1(z_1)K_1^{(+)}(z_1), \tag{46}$$

$$\delta_T = \frac{T}{\sigma_0}\int dn_1(z_1)z_1 K_1^{(-)}(z_1). \tag{47}$$

The odd part $\mathcal{K}_1(z_1)$ due to (28) can be connected with the asymmetric contribution to the compressibility. In view of (28), Eq.(41) can be written as

$$C_2(n;\mathbf{r}_{12}) \propto |\tau|^{2-\alpha+\gamma}\left(1 + c|\tau|^\beta + ...\right),$$

where c is a temperature-independent coefficient. Following the same estimates as in (36) for (38), we easily obtain the leading term $|\tau|^{\beta-\nu}$. Another correction can be obtained in the same way. Thus, we see that the Tolman length is intrinsically connected with the asymmetry of the correlation functions and the microscopic Hamiltonian.

We finish our analysis by making connection of the above results with the Fisher–Wortis representation for δ_T:

$$\delta_n = \frac{\int\limits_{-\infty}^{+\infty} zn'(z)dz}{\int\limits_{-\infty}^{+\infty} n'(z)dz} - \frac{\int\limits_{-\infty}^{+\infty} zn'^2(z)dz}{\int\limits_{-\infty}^{+\infty} n'^2(z)dz}, \tag{48}$$

where $n(z)$ is the equilibrium density profile of the coexisting phases. This representation was derived on the basis of the Landau–Ginzburg functional [11]. Using the result of the previous section, we perform the inverse local canonical transformation:

$$\tilde{n}(\mathbf{r}) = \eta(\mathbf{r}) - \frac{1}{2}\Gamma_2\eta^2(\mathbf{r}) + o\left(\eta^2(\mathbf{r})\right), \tag{49}$$

where $\tilde{n} = n(\mathbf{r})/n_c - 1$. This transformation restores the symmetry of the thermodynamic functional in terms of the canonical variable η, as was shown in Section 2 (see (25)). By definition, the spatial profile of the canonical order parameter $\eta_0(z)$ is an odd function with respect to the interphase boundary $z = 0$ defined as the "equi-η" surface:

$$\eta_0(-z) = -\eta_0(z), \tag{50}$$

just like for any model with the even Landau–Ginzburg functional [11]. It follows from (25) that the phase coexistence profile of the density can be written as

$$\tilde{n}(z) = \eta_0(z) + \eta_{\mathrm{asym}}(z) + o\left(\eta_0^2(z)\right)$$

with the obvious Ising-like properties

$$\eta_0(z) = -\eta_0(-z), \quad \eta_{a\mathrm{sym}}(z) = \eta_{a\mathrm{sym}}(-z). \tag{51}$$

Substituting this expression into (48), we obtain

$$\delta_T = -\Gamma_2 \delta_{\mathrm{can}} + o\left(\eta_0^2\right), \tag{52}$$

where

$$\delta_{\mathrm{can}} = \delta_\eta + \delta_s. \tag{53}$$

Thus, the amplitude value of the Tolman length is governed by the value of Γ_2, which can be either positive or negative, depending on the details of the microscopic interaction. Asymptotically, $\eta_0 \propto |\tau|^\beta$ and $\eta_{a\mathrm{sym}} \propto |\tau|^{2\beta}$, so we can write

$$\delta_\eta = \frac{1}{2}\frac{\int\limits_{-\infty}^{+\infty} z d\eta_0^2(z)}{\int\limits_{-\infty}^{+\infty} d\eta_0(z)} - 2\frac{\int\limits_{-\infty}^{+\infty} z\eta_0(z)\eta_0'^2(z)dz}{\int\limits_{-\infty}^{+\infty} \eta_0'^2(z)dz}, \tag{54}$$

$$\delta_s = \frac{1}{2}\frac{\int\limits_{-\infty}^{+\infty} z ds_\eta(z)}{\int\limits_{-\infty}^{+\infty} d\eta_0(z)} - \frac{\int\limits_{-\infty}^{+\infty} z s_\eta'(z) d\eta_0(z)}{\int\limits_{-\infty}^{+\infty} \eta_0'^2(z)dz}, \tag{55}$$

where $\eta(z)$ and $s_\eta(z)$ are the equilibrium profiles of the canonical order parameter and the entropy, correspondingly. Since the density profile varies over the correlation length ξ, which is the only relevant characteristic spatial scale near the CP, then the simple scaling consideration gives

$$\delta_\eta \propto \tau^{\beta-\nu}, \quad \delta_s \propto \tau^{1-\alpha-\beta-\nu}. \tag{56}$$

Thus, all expressions lead to the same leading critical behavior. Note that it is the canonical representation (26), which leads to the correct result even in the square gradient approximation used in the derivation of (48). This is in contrast to the inadequacy of the square gradient approximation for the surface tension (44) which uses on the non-canonical order parameter.

Expression (52) for the Tolman length allows us to shed light on the nature of the approximate relation between δ_T and the density diameter $n_d = \frac{n_{\mathrm{liq}}+n_{\mathrm{gas}}}{2n_c}$:

$$\delta_T \simeq -\xi\frac{n_d - 1}{\Delta n}, \tag{57}$$

which was proposed in [22]. In fact, this relation expresses the fact that both δ_T n_d has the same origin – the asymmetry of the Hamiltonian in terms of the initial order parameter, which is not canonical. In the canonical formalism, both these quantities are proportional to the same asymmetry factor Γ_2 according to (26) and Eqs. (52),(53).

4. Conclusion

We have performed the detailed analysis of the asymptotic behavior of the Tolman length near the CP of a molecular liquid. Within the ideology of the canonical form for the fluctuational Hamiltonian (see [18–20]), it is the trivial fact that the non-zeroth value of the Tolman length is the effect of the asymmetry of the Hamiltonian. In such a way, the relation between the critical amplitudes and the coefficients of the initial Hamiltonian is obtained. With the help of the transformation to the canonical order parameter, we derive the invariant representation of the Tolman length in terms of the profiles of the canonical order parameter and the canonical entropy. The leading singular terms are generated by these two contributions and are proportional to $\propto \tau^{\beta-\nu}$ and $\propto \tau^{1-\alpha-\beta-\nu}$ correspondingly. This is in agreement with the results of [22, 23] based on the "complete scaling" approach [21]. It uses the assumption about three scaling fields for the critical behavior of molecular liquids. Within the canonical approach, we adhere to the fact that there is only two fluctuating fields for the molecular liquids [51]. In addition, the method of [23] works with the truncated Landau expansion of the free energy. In contrast to it, the technique of canonical forms for the fluctuational Hamiltonian allows one to operate with the whole expansion. Moreover, there is a profound relation between the procedure of canonical transformation and the global isomorphism approach [17, 52]. The latter also uses a transformation that makes the binodal symmetric. One can consider the projected transformations [52] as the mean-field version of the canonical transformation beyond the critical region. This route is worth of the further development.

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APPENDIX A
The Canonical Transformation for the Density Profile

The rigorous mathematical approach to the existence of the canonical transformation in the case of the infinite number of variables is not developed yet. Here, we give an indirect evidence for the existence of the canonic transformation, by considering the density profile of the phase coexistence.

Let us consider the inhomogeneous equilibrium state of the liquid-vapor system with planar interface. Let $n(z)$ be the density profile. The latter is nothing but the one-particle distribution function. Evidently, $n(z)$ has the asymptotes:

$$\tilde{n}(z) = \begin{cases} n_l, z \to +\infty, \\ n_g, z \to -\infty. \end{cases} \tag{A1}$$

Let us subtract the background constant and use the excess density

$$n(z) = \begin{cases} n_l - n_g, z \to +\infty, \\ 0, z \to -\infty. \end{cases} \tag{A2}$$

If the profile is monotonic, then we can interpret $n(z)$ as a distribution function for some measure with $n'(z) > 0$ as the measure density. Then the Radon–Nikodim theorem assures the existence of the transformation to the profile corresponding to functional (17).

In general, $n(z)$ can be non-monotonic or even oscillatory, as in the case of liquid metals [53]. Then we can define the functional

$$F_n(z) = \frac{1}{h_n(z)} \int\limits_{-\infty}^{z} n(x)dx > 0. \tag{A3}$$

The functional $h_n(z) > 0$ is chosen in such a way that $F_n(z)$ is monotonic in z and bounded:

$$\frac{d}{dz} \ln F_n(z) = \frac{n(z)}{\int\limits_{-\infty}^{z} n(x)dx} - \frac{h_n'(z)}{h_n(z)} > 0. \tag{A4}$$

As a minorant in a sense of (A4), it is possible to take $h_n(z)$ in the form

$$h_n(z) = \exp\left(\int\limits_{-\infty}^{z} dx \frac{\tilde{n}(x)}{1 + \tilde{n}'(x)^2} \right),$$

where

$$\tilde{n}(x) = \frac{n(x)}{\int\limits_{-\infty}^{x} dy n(y)}.$$

Therefore, the functional F_n given by (A3) can be interpreted as the measure corresponding to the profile $n(z)$ even if $n(z)$ is not monotonic. Then the Radon–Nikodim theorem holds for F_n.

This means that, for any profile $n(z)$, we can choose the smooth invertible local transformation (diffeomorphism) $\eta(z) = f(n(z))$ so that the profile $\eta(z)$ corresponds to the canonical functional (17). Note that while $n(z)$ is determined by both nonlocal and local parts of the system's Hamiltonian, this interpretation of the canonical transformation is independent of a particular form of these parts and uses only the general property (A2).

1. R.C. Tolman, J. Chem. Phys. **17**(3), 333 (1949).
2. W. Helfrich, Z. Naturforsch. C **28**, 693 (1973).
3. J.S. Rowlinson and B. Widom, *Molecular Theory of Capillarity* (Claredon Press, Oxford, 1982).
4. A. Dillmann and G.E.A. Meier, J. Chem. Phys. **94**, 3872 (1991).
5. C.F. Delale and G.E.A. Meier, J. Chem. Phys. **98**, 9850 (1993).
6. V.I. Kalikmanov, Phys. Rev. E **55**, 3068 (1997).
7. M.E. Fisher, Physics **3**, 255 (1967).
8. L.A. Bulavin, O.A. Grekhov, and V.M. Sysoev, J. Surf. Invest. X Ray **4**, 74 (1998).
9. V.M. Kolomietz and A.I. Sanzhur, Phys. Rev. C **88**, 044316 (2013).
10. K.V. Cherevko, L.A. Bulavin, L.L. Jenkovszky, V.M. Sysoev, and F.-S. Zhang, Phys. Rev. C **90**, 017303 (2014).
11. M.P.A. Fisher and M. Wortis, Phys. Rev. B **29**, 6252 (1984).
12. P. Phillips and U. Mohanty, J. Chem. Phys. **83**, 6392 (1985).
13. A.Z. Patashinskii and V.L. Pokrovsky, *Fluctuation Theory of Critical Phenomena* (Pergamon, Oxford, 1979).
14. J.F. Nicoll, Phys. Rev. A **24**, 2203 (1981).
15. V.L. Kulinskii, J. Chem. Phys. **133**, 034121 (2010).
16. L.A. Bulavin and V.L. Kulinskii, J. Chem. Phys., **133**, 134101 (2010).
17. L.A. Bulavin and V.L. Kulinskii, J. Phys. Chem. B **115**, 6061 (2011).
18. V.L. Koulinskii and N.P. Malomuzh, Condens. Matter Phys. **9**, 29 (1997).
19. V.L. Kulinskii, J. Mol. Liq. **105**, 273 (2003).
20. V. Kulinskii and N. Malomuzh, Physica A **388**, 621 (2009).
21. Y.C. Kim, M.E. Fisher, and G. Orkoulas, Phys. Rev. E **67**, 061506 (2003).
22. M.A. Anisimov, Phys. Rev. Lett. **98**, 035702 (2007).
23. J. Wang and M.A. Anisimov, Phys. Rev. E **75**, 051107 (2007).
24. E.M. Blokhuis and J. Kuipers, J. Chem. Phys. **124**, 074701 (2006).
25. M.A. Anisimov and J. Wang, Phys. Rev. Lett. **97**, 025703 (2006).
26. J. Hubbard and P. Schofield, Phys. Lett. A **40**, 245 (1972).
27. M.F. Holovko and I.R. Yukhnovsky, *The Statistical Theory of Classical Equilibrium Systems* (Naukova Dumka, Kyiv, 1980) (in Russian).
28. V.L. Kulinskii, Ukr. Fiz. Zh. **38**, 1872 (1993).
29. L.D. Landau and E. M. Lifshitz, *Statistical Physics, Part 1* (Pergamon Press, Oxford, 1980).

30. T. Poston and I.N. Stewart, *Catastrophe Theory and Its Applications* (Pitman, London, 1978).
31. R. Gilmore, *Catastrophe Theory for Scientists and Engineers* (Wiley, New York, 1981), Vol. 1.
32. V.I. Arnold, A.N. Varchenko, and S.M. Gusein-Zade, *Singularities of Differentiable Maps: Vol. 1: The Classification of Critical Points Caustics, Wave Fronts* (Birkhäuser, Boston, 1985).
33. N. Dunford and J.T. Schwartz, *Linear Operators, General Theory* (Wiley-Interscience, New York, 1988), Vol. 1.
34. D. Sornette, P. Simonetti, and J.V. Andersen, Phys. Rep. **335**, 19 (2000).
35. Yu.M. Ivanchenko, A.A. Lisyansky, and A.E. Filippov, *Fluctuational Effects in the Systems with Competitive Interactions* (Naukova Dumka, Kiev, 1989) (in Russian).
36. M. Abramovitz and I.A. Stegun, *Handbook of Mathematical Functions with Formulas, Graphs, and Mathematical Tables* (Dover, New York, 1972).
37. J.F. Nicoll and R.K.P. Zia, Phys. Rev. B **23**, 6157 (1981).
38. Y.C. Kim and M.E. Fisher, Chem. Phys. Lett. **414**, 185, (2005).
39. V.C. Weiss and W. Schröer, J. Stat. Mech. **2008**, P04020 (2008).
40. C.N. Yang and C.P. Yang, Phys. Rev. Lett. **13**, 303 (1964).
41. M.E. Fisher, J. Stat. Phys. **75**, 1 (1994).
42. L.A. Bulavin, V.L. Kulinskii, and N.P. Malomuzh, Ukr. Fiz. Zh. **55**, 1238 (2010).
43. S. Fisk and B. Widom, J. Chem. Phys. **50**, 3219 (1969).
44. E.M. Blokhuis and J. Kuipers, J. Chem. Phys. **126**, 054702 (2007).
45. E.M. Blokhuis and D. Bedeaux, J. Mol. Phys. **80**, 705 (1993).
46. J.G. Kirkwood and F.P. Buff, J. Chem. Phys. **17**, 338 (1949).
47. E.M. Blokhuis and D. Bedeaux, J. Chem. Phys. **97**, 3576 (1992).
48. J.-P. Hansen and I.R. Mcdonald, *Theory of Simple Liquids* (Academic Press, New York, 2006).
49. D.G. Triezenberg and R. Zwanzig, Phys. Rev. Lett. **28**, 1183 (1972).
50. E.M. Blokhuis, Phys. Rev. E **87**, 022401 (2013).
51. V.L. Kulinskii and N.P. Malomuzh, J. Mol. Liq. **158**, 166 (2011).
52. V.L. Kulinskii, J. Phys. Chem. B **114**, 2852 (2010).
53. S.W. Barton, B.N. Thomas, F. Novak, P.M. Weber, J. Harris, P. Dolmer, J.M. Bloch, and S.A. Rice, Nature **321**, 685 (1986).

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АСИМЕТРІЯ ГАМІЛЬТОНІАНА
І СИНГУЛЯРНА ПОВЕДІНКА ДОВЖИНИ ТОЛМЕНА
В РАМКАХ КАНОНІЧНОГО ФОРМАЛІЗМУ

Р е з ю м е

В статті розглядається зв'язок асиметрії гамільтоніана з критичною поведінкою довжини Толмена на основі нелінійного перетворення параметра порядку. Показано, що структура критичної асимптотики цієї величини збігається з такою для асиметричної частини ізотермічної стисливості. Взаємозв'язок сингулярності діаметра бінодалі і толменівської довжини обґрунтовано в рамках формалізму канонічної форми гамільтоніана. Показано яким чином головні асимптотичні члени можуть бути отримані на основі точних виразів статистичної механіки для довжини Толмена. Результати порівнюються із відомими результатами роботи M.A. Anisimov, Phys. Rev. Lett. **98**, 035702 (2007).