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Geometrical Aspect of Compressibility Critical Exponent

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Critical exponent $\gamma \ge 1.1$ characterizes the behavior of the mechanical compressibility of a real fluid when the temperature approaches the critical one. It results in zero Gaussian curvature of the local shape of the critical point on the thermodynamic equation of state surface, which imposes a new constraint upon the construction of the potential equation of state of the real fluid from the empirical data. All known empirical equations of the state suffer from a weakness that the Gaussian curvature of the critical point is negative definite instead of zero.

Keywords: critical point, critical exponent, fluid system, Gaussian curvature, equation of state

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It is believed that God created the universe according to a geometric plan, and geometry is everywhere. Physics is the most fundamental scientific discipline with its main goal to understand the universe, and geometry is deeply rooted in every branch of physics. The present work concentrates on the relationship between thermodynamics and geometry. The modern version of thermodynamics can be reformulated in terms of contact geometry [1], and the so-called geometry of thermodynamics has been put forward, which describes the space of thermodynamic parameters by the Riemannian metric [2–4]. The influence of the curved space on the critical behavior of the two-dimensional Ising model is identified [5], and geometric critical exponents are definable in classical and quantum phase transitions [6]. Latest advances include the geometrical methods employed in the analysis of quantum phase transitions and non-equilibrium dissipative phase transitions [7], the new formalism of thermodynamic geometry employed in investigating phase transition points, and the critical behavior of a Gauss–Bonnet-AdS black hole in four-dimensional spacetime [8]. Thus, the new relationship between thermodynamics and geometry is always interesting, and we report a new requirement on the construction of the empirical equation of state (EoS) based on the differential geometry of the surfaces.

The elaboration of a form of the empirical EoS best fitting the experimental data and also meeting the theoretical requirements has been an important issue for more than one century [9–15]. For a real fluid, an open theoretical problem is, in the close neighborhood of the critical point, what is the better form of the EoS? For instance, it is well-known that both the van der Waals EoS and the general theory of the Landau theory of phase transitions predict the compressibility critical exponent $\gamma = \gamma'$ to be 1, and all known empirical EoS fail to exactly reproduce the experimental values $\gamma = 1.2 \sim 1.3 \gtrsim \gamma' = 1.1 \sim 1.2$ [16, 17]. Recently, we have conjectured that the Gaussian curvature of the local shape of the vapor-liquid critical point is zero [18]. In the present study, we first prove that the conjecture is true and secondly report the construction of a fluid EoS, which has $\gamma = \gamma' = 3$, which is quantitatively different from the experimental values but leads to the zero Gaussian curvature of the vapor-liquid critical point.

The fluid of a pure substance belongs to the so-called pVT system, which means that the EoS usually takes following simplest form:

$$p = p(V, T), \tag{1}$$

where p, V, T denote the pressure, volume, and temperature, respectively. In general, at the critical point (p_c, V_c, T_c), the first- and second-order derivatives of the EoS (1) are continuous and their values are zero:

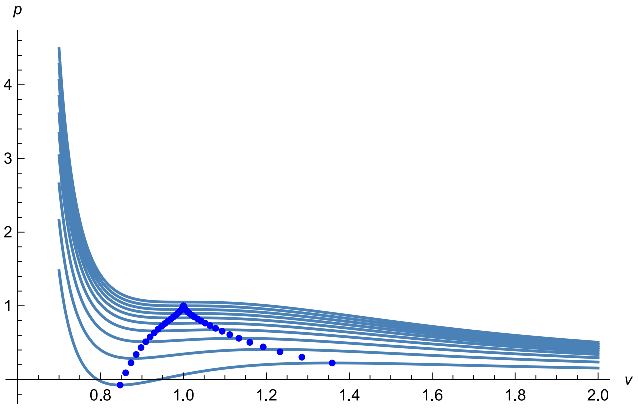

FIGURE 1 | The isotherms (solid lines) with $T = 0.60, 0.65, 0.70, \ldots, 1.05$ from undermost to upmost, and the spinodal curve (solid dots) for EoS (11). The EoS captures the essential feature of the vapor-liquid phase transition for the existence of the van der Waals loops, clearly indicating a first-order phase transition in the liquid system.

$$\left(\frac{\partial p}{\partial V}\right)_{T_c} = 0, \left(\frac{\partial^2 p}{\partial V^2}\right)_{T_c} = 0. \tag{2}$$

In other words, the values (p_c, V_c, T_c) can be determined by an association of three **Eqs 1**, **2**. In present study, we do not deal with piecewise or other discontinuous form of EoS (1).

In geometry, the EoS (1) can be viewed as a two-dimensional surface in the flat pVT space, and its shape can be completely characterized by the mean and the Gaussian curvature [19]. It is then interesting to explore the local shape of the vapor-liquid critical point *via* these two curvatures. In calculation, the dimensionless EoS surface **Equation 1** must be used, in which all quantities (p, V, T) are transformed into those referring to units (p_c, V_c, T_c) or other units (p', V', T') of a specific state. The transformed form of EoS bears a resemblance to the law of corresponding states of the van der Waals EoS. The mean curvature H and Gaussian curvature K are, respectively [19],

$$H = \frac{\left(\frac{\partial^2 p}{\partial V^2}\right)_T \left(\left(\frac{\partial p}{\partial T}\right)_V^2 + 1\right) + \left(\frac{\partial^2 p}{\partial T^2}\right)_V \left(\left(\frac{\partial p}{\partial V}\right)_T^2 + 1\right) - 2\left(\frac{\partial p}{\partial V}\right)_T \left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial^2 p}{\partial V \partial T}\right)}{2\left(\left(\frac{\partial p}{\partial V}\right)_T^2 + \left(\frac{\partial p}{\partial T}\right)_V^2 + 1\right)^{3/2}}, \tag{3}$$

$$K = \frac{\left(\frac{\partial^2 p}{\partial V^2}\right)_T \left(\frac{\partial^2 p}{\partial T^2}\right)_V - \left(\frac{\partial^2 p}{\partial V \partial T}\right)^2}{\left(\left(\frac{\partial p}{\partial V}\right)_T^2 + \left(\frac{\partial p}{\partial T}\right)_V^2 + 1\right)^2}. \tag{4}$$

At the critical point, conditions (2) apply, and we have the mean curvature H_C and the Gaussian curvature K_C, respectively:

$$H_C = \frac{\left(\frac{\partial^2 p}{\partial T^2}\right)_V}{2\left(\left(\frac{\partial p}{\partial T}\right)_V^2 + 1\right)^{3/2}}, K_C = -\frac{\left(\frac{\partial^2 p}{\partial V \partial T}\right)^2}{\left(\left(\frac{\partial p}{\partial T}\right)_V^2 + 1\right)^2}. \tag{5}$$

The compressibility or a mechanical response function,

$$\kappa_T \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T, \tag{6}$$

leads to

$$\left(\frac{\partial p}{\partial V}\right)_T = -\frac{1}{V \kappa_T}. \tag{7}$$

Near the critical point, the experiments suggest, with $\gamma \approx \gamma' \sim 1.2$ [16, 17],

$$\kappa_T \propto \left\{ \begin{array}{ll} (T - T_c)^{-\gamma}, & (T \to T_c + 0) \\ (T_c - T)^{-\gamma'}, & (T \to T_c - 0) \end{array} \right. . \tag{8}$$

In consequence, we have

$$\frac{\partial^2 p}{\partial V \partial T} = -\frac{1}{V}\frac{\partial}{\partial T}\left(\frac{1}{\kappa_T}\right) \propto \left\{ \begin{array}{ll} (T - T_c)^{\gamma - 1}, & (T \to T_c + 0) \\ (T_c - T)^{\gamma' - 1}, & (T \to T_c - 0) \end{array} \right. = 0, \tag{9}$$

which can be rewritten into the following, in terms of the Gaussian curvature from **(5)**:

$$K_C = 0. \tag{10}$$

Thus, for real fluids, the Gaussian curvature of the local shape of the critical point of the EoS surface is zero.

In contrast, all known empirical EoS at the critical point give the negative values of the Gaussian curvature $K_C \prec 0$, whose typical results are listed in **Table 1**, from which we see that none of them can reproduce $K_C = 0$. In the last line of **Table 1**, the Shamsundar–Lienhard EoS [14] is special, because it is a principle ("The shape of the (experimental data) figure tells us that a cubic-like equation must be of the form" [14]) rather than an explicit form of an EoS. Though these empirical EoS in **Table 1** do not exhaust all possibilities, we are safe to say that $K_C = 0$ is beyond the current form of the Landau theory of phase transitions because it generally predicts $\gamma = \gamma' = 1$, thus $K_C \prec 0$ for $(\partial^2 p / \partial V \partial T)_c =$ *const* at the critical point (p_c, V_c, T_c) [16, 17].

Now, we present an EoS with $K_C = 0$. Our constructed EoS takes following form:

$$p = \frac{8T}{9\left(V - \frac{1}{3}\left(\frac{19}{3} - \frac{6}{V} + \frac{2}{V^2}\right)\right)} - \frac{3\left(3 - \frac{3}{T} + \frac{1}{T^2}\right)}{V^2}, \tag{11}$$

where (p, V, T) are written in unit $(p_c, V_c, T_c)(= (1, 1, 1))$. It can be considered a highly distorted version of law of corresponding state of the van der Waals equation. The isotherms given by this EoS (11) are plotted in **Figure 1**. Below the critical temperature T_C, the isotherms explicitly exhibit van der Waals loops. Straightforward calculations show that both the mean and the Gaussian curvature at the critical point are zero, that is, $H_C = K_C = 0$, and also a symmetrical compressibility critical exponent:

$$\gamma = 3\ (T \to T_C + 0), \text{and}\ \gamma' = 3\ (T \to T_C - 0). \tag{12}$$

It is quantitatively different from the compressibility critical exponent for the real fluid. The origin of the difference may

TABLE 1 | Mean and Gaussian curvature of the critical points for empirical or semi-empirical EoS. Symbol *v* denotes the molar volume, *a* and *b* are repulsive and attractive parameters, respectively, $y = b/4v$, and $a(T)$ depends on temperature and other substance parameters [9, 15]. Only one typical value of the substance parameter in $a(T)$ is used in the calculations.

No.	References	EoS	H_C	K_C	Year
1	van der Waals	$\frac{RT}{v-b} - \frac{a}{v^2}$	0	−0.125	1873
2	Dieterici	$\frac{RT}{v-b} \exp\left(-\frac{a}{vkT}\right)$	0.063	−0.04	1916
3	Redlich–Kwong	$\frac{RT}{v-b} - \frac{a}{T^{1/2} v(v+b)}$	−0.006	−0.065	1949
4	Thiele	$\frac{RT}{v} \frac{1+y+y^2}{(1-y)^3} - \frac{a}{v^2}$	0	−0.099	1963
5	Guggenheim	$\frac{RT}{v} \frac{1}{1-y^4} - \frac{a}{v^2}$	0	−0.101	1965
6	Carnahan–Starling	$\frac{RT}{v} \frac{1+y+y^2-y^3}{(1-y)^3} - \frac{a}{v^2}$	0	−0.099	1969
7	Soave	$\frac{RT}{v-b} - \frac{a(T)}{v(v+b)}$	−0.004	−0.045	1972
8	Peng–Robinson	$\frac{RT}{v-b} - \frac{a(T)}{v(v+b)+b(v-b)}$	−0.003	−0.058	1976
9	Shamsundar–Lienhard	$g(T)\left(1 - \frac{(V-V_l)(V-V_m)(V-V_g)}{f(V,T)}\right)$[a]	—	0	1993

[a] *In this EoS, symbols* g(T), V_l, V_m, V_g *stand for four parameters depending on the temperatures, and* f (V, T) *depends on both volume and temperature and possesses no poles or roots in the physical range of* V. *The explicit form of* f (V, T) *depends on other three parameters, details of which do not affect our conclusion.*

lie in that we use the continuous form of the EoS rather than the discontinous ones, which shall be explored in the future.

So far, there are at least three requirements in the form of EoS for the real fluid: 1) in large volume limit, the EoS reproduces the ideal gas law [14]; 2) at both ends of a vapor-liquid coexistence line, there are onset and outset value for volume for gas and liquid state and a coexisting pressure [14]; and 3) the Gaussian curvature of the critical point is zero. All these constraints directly come from experiments. There may be other constraints on the form of the EoS, which may arise from the theoretical requirements, such as Maxwell area construction for the van der Waals loop [14], which must nevertheless be used case by case.

In summary, geometry not only offers a better understanding and deeper insight into the mathematical structure of thermodynamics but also presents an accurate and convenient means to characterize various properties of thermodynamic states. We report that the local shape of the vapor-liquid critical point on the thermodynamic surface has zero Gaussian curvature, which has long been hidden in the compressibility critical exponent $\gamma > 1$. It can be used to distinguish different empirical models and impose this requirement on the construction of the new EoS. A new form of the EoS capturing the essential feature of the vapor-liquid phase transition with $\gamma > 1$ is successfully elaborated. Without explicitly carrying it out, we are confident that the theoretical value $\gamma = \gamma' = 3$ for the compressibility critical exponent can be explained within the higher order of the Landau theory of phase transitions.

DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/Supplementary Material. Further inquiries can be directed to the corresponding author.

AUTHOR CONTRIBUTIONS

JY and QL contributed to the conception and design of the study. WD organized the database. QL wrote the first draft of the manuscript. All authors contributed to manuscript revision and read and approved the submitted version.

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