Local shape of the vapor-liquid critical point on the thermodynamic surface and the van der Waals equation of state

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Differential geometry is powerful tool to analyze the vapor-liquid critical point on the surface of the thermodynamic equation of state. The existence of usual condition of the critical point \((\partial p/\partial V)_T = 0\) requires the isothermal process, but the universality of the critical point is its independence of whatever process is taken, and so we can assume \((\partial p/\partial T)_V = 0\). The distinction between the critical point and other points on the surface leads us to further assume that the critical point is geometrically represented by zero Gaussian curvature. A slight extension of the van der Waals equation of state is to letting two parameters \(a\) and \(b\) in it vary with temperature, which then satisfies both assumptions and reproduces its usual form when the temperature is approximately the critical one.

Keywords: critical point, van der Waals equation of state, Gaussian curvature, saddle point, response functions

I. INTRODUCTION

In thermal physics, a critical point is the end point of a phase equilibrium curve, the pressure–temperature curve that designates conditions under which a liquid phase and a vapor phase can coexist. The critical point \((T_C, V_C, p_C)\) in the \(pV\) diagrams determined by,

\[
\left(\frac{\partial p}{\partial V}\right)_T = 0, \quad \left(\frac{\partial^2 p}{\partial V^2}\right)_T = 0,
\]

(1)
together with the thermodynamic equation of state (EoS), where symbols \((T, V, p)\) have their usual meaning in ordinary textbooks [1–5]. The phase transition exhibits critical slowing down, universality and scaling, etc., which reflect a fact that the details of the system play insignificant role [6, 7]. How to characterize the essence of the critical point is always an attractive topic. We note two seemingly independent developments/facts. One is that the critical slowing down is its path-independence [8–12], which means that starting from any thermodynamic state in the vicinity of a critical point to approach to it, the system has inherently slow timescales whatever thermodynamic processes are chosen. The second is that a geometrical description of a local point on a curved surface is irrespective of either the parameters chosen to label the point of the surface or the paths selected to approach to it. The strong resemblance of these two facts suggests that geometrical description of the critical point is advantageous. Based on this observation, we make a proposal that the critical point is geometrically represented by zero Gaussian curvature on the thermodynamic EoS surface, together with some physical assumptions. We hope to use this proposal to resolve a long standing problem associated with the van der Waals (vdW) EoS.

The most prominent aspect of the vdW EoS is that it captures many of the qualitative features of the liquid–vapor phase transition with possible help of Maxwell’s equal area rule. The vdW EoS was essentially presented [13] (but explicitly given later [14]) by van der Waals in his 1873 Ph. D. thesis, and for this he was awarded the Nobel Prize in Physics 1910 [15, 16]. The vdW EoS is well-known,

\[
p = \frac{nRT}{V-nb} - \frac{n^2a}{V^2},
\]

(2)

where two parameters, \(a\) and \(b\), can be estimated from the critical point and considered constants which are specific for each substance, and other symbols \((n, R)\) also have their usual meaning in ordinary textbooks [1, 2]. For one mole fluid \(n = 1\), and the values of \(T_C, V_C, p_C\) are in terms of \(a\) and \(b\) parameter [1, 2],

\[
T_C = \frac{8a}{27Rb}, \quad p_C = \frac{a}{27b^2}, \quad V_C = 3b.
\]

(3)

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With these values, the vdW EoS can be transformed into following dimensionless form,

\[ p^* = \frac{8}{3} \frac{t^*}{v^* - 1/3} - \frac{3}{v^*2}, \]

where,

\[ t^* = \frac{T}{T_C}, \quad v^* = \frac{V}{V_C}, \quad p^* = \frac{p}{p_C}. \]

The equation (4) is referred as the Law of Corresponding States which holds for all kinds of fluid substances, which was also originated with the work of van der Waals in about 1873 [13], when he used the critical temperature and critical pressure to characterize a fluid. However, whether and how the vdW parameters \(a\) and \(b\) depend on the temperature \(T\), and even more, on the volume \(V\), has been a problem of long history. van der Waals himself was well-aware of it [14], and remarked in his Nobel prize speech: "I have never been able to consider that the last word had been said about the equation of state and I have continually returned to it during other studies. As early as 1873 I recognized the possibility that \(a\) and \(b\) might vary with temperature, and it is well-known that Clausius even assumed the value of \(a\) to be inversely proportional to the absolute temperature." [13] In fact, more than one century passed since the discovery of the vdW EoS, we do not have a strong experimental evidence nor a compelling theoretical argument to indicate how \(a\) and \(b\) parameter might depend on the temperature and/or volume. We have some theoretical results in statistical mechanics, revealing some temperature dependence of \(a\) and \(b\), for instance in the hard-sphere model [1-3], but these results are frequently obtained for dilute fluid far from the critical point, and more importantly, they rely heavily on the specific model without universality which is inherent to the thermodynamics.

The present paper thus addresses two problems. One is why we assume \((\partial p/\partial T)_V = 0\) that is complementary to the first equation of (1), and why we propose that the critical point is geometrically represented by zero Gaussian curvature on the thermodynamic EoS surface. Another is to use above assumptions to discuss the long-standing problem within the thermodynamics. The paper is organized in the following. In section II, we prove a theorem stating that the local shape of the vapor-liquid critical point on the thermodynamic surface can never be an elliptic point; and in order to completely characterize the local shape of the critical point, we need two more response functions which are assumed to vanish at the critical point, implied by the critical slowing down observed in either the realistic experiments or the computer simulation of the phase transition [8,12]. The vanishing response functions leads to the zero Gaussian curvature. In section III, the vdW EoS is slightly extended such that the parameters \(a\) and \(b\) vary with the temperature \(T\), which is thus capable to give zero Gaussian curvature at the critical point, while the usual form of the vdW EoS fails. In section IV, a brief summation of the present study is given.

In present paper, we concentrate the (interior) Gaussian curvature that is sufficient to specify the local shape of the two-dimensional thermodynamic EoS surface, but we will also give the (exterior) mean curvature as a contrasting quantity. In geometry, the curvature is usually referred to the interior one.

II. LOCAL SHAPE OF THE VAPOR-LIQUID CRITICAL POINT ON THE EOS SURFACE AND A PROPOSAL

In differential geometry, the local shapes of a two-dimensional curved surface are completely classified into three types: elliptic, hyperbolic and parabolic, corresponding to the Gaussian curvature greater than, smaller than or equal to, zero, respectively [20]. For a thermodynamic EoS \(p = p(T, V)\) that can be treated as a two-dimensional surface in the three-dimensional flat space of coordinates \(p, T \) and \(V\), we now show that the vapor-liquid critical point can not be an elliptic point.

In geometry, it is preferable to use the dimensionless equation of the EoS surface \(p = p(T, V)\). The straightforward calculations can, respectively, give \(H\) and Gaussian curvature \(K\),

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

\[ K = \frac{\left(\frac{\partial^2 p}{\partial V^2}\right)_T \left(\frac{\partial^2 p}{\partial T^2}\right)_V - \left(\frac{\partial^2 p}{\partial V \partial T}\right)_V^2}{\left(\frac{\partial p}{\partial V}\right)_T^2 + \left(\frac{\partial p}{\partial T}\right)_V^2 + 1\right)^2}. \]
At the critical point the conditions \(^{(1)}\) apply, we have the mean curvature \(H_C\) and Gaussian curvature \(K_C\), respectively,
\[
H_C = \frac{\left( \frac{\partial^2 p}{\partial V^2} \right)_V}{2 \left( \left( \frac{\partial p}{\partial V} \right)_V \right)^2 + 1}^{3/2}, \quad K_C = -\frac{\left( \frac{\partial^2 p}{\partial T^2} \right)_V^2}{\left( \left( \frac{\partial p}{\partial T} \right)_V \right)^2 + 1},
\]
which shows that \(K \leq 0\). Thus, we in fact prove a theorem that the local shape of the vapor-liquid critical point on the thermodynamic surface can never be an elliptic point.

To illustrate the mean and Gaussian curvature of the surface of the thermodynamic EoS, let us first consider two simple systems. For an incompressible liquid EoS: \(V = \text{const.}\), which is a flat plane, both curvatures are zero. The ideal gas EoS surface, \(p = nRT/V\) which can be rewritten as a dimensionless one \(p^*/v^* = t^*\) with a reference point \((p_0, V_0, T_0 (= p_0 V_0 / (nR)))\), where \(t^* \equiv T/T_0, v^* \equiv V/V_0, p^* \equiv p/p_0\). The mean curvature \(H\) and Gaussian curvature \(K\) are, respectively,
\[
H = \frac{t^* v^*^3}{(t^*^2 + v^*^2 + v^*^4)^{3/2}}, \quad K = -\frac{v^*^4}{(t^*^2 + v^*^2 + v^*^4)^2},
\]
Since the Gaussian curvature \(K < 0\) is negative definite, every point on the ideal gas EoS surface is saddle.

Now, we examine vdW EoS surface \(^{(2)}\) and it is preferable to use the dimensionless form \(^{(4)}\). The mean curvature \(H\) and Gaussian curvature \(K\) are, respectively,
\[
H = 9v^*^5(3v^* - 1)^3 \frac{F_1(t^*, v^*)}{(F_2(t^*, v^*))^{3/2}}, \quad K = -\frac{576(3v^* - 1)^4v^{*12}}{(F_2(t^*, v^*))^2},
\]
where,
\[
F_1(t^*, v^*) = 8t^*^4v^{*4} - 27v^*^3 + 27v^*^2 - 73v^* + 65,
F_2(t^*, v^*) = 576t^*^2v^{*6} - 2592t^*v^{*5} + 1728t^*v^{*4} - 288t^*v^{*3} + 81v^{*10} - 108v^{*9} + 630v^{*8} - 396v^{*7} + 65v^{*6} + 2916v^{*4} - 3888v^{*3} + 1944v^{*2} - 432v^* + 36.
\]
At the critical point \((t^*, v^*) = (1, 1)\), we have, respectively,
\[
H_C = 0, \quad K_C = -\frac{36}{289} \approx -0.125.
\]
The negative Gaussian curvature \(K_C \approx -0.125\) indicates that the critical point is a hyperbolic point, more precisely, a saddle point \(^{(20)}\).

A comparison of the Gaussian curvatures \(^{(9)}\) for ideal gas and \(^{(13)}\) for vdW EoS suggests that there is no qualitative difference in between. It is a little bit odd, for we believe that a realistic EoS differs from the ideal gas EoS in the qualitative sense, rather than a quantitative one. By the critical point on the PV diagram, we mean a stationary inflection point in the constant-temperature line, critical isotherm, whose location is determined by two equations in \(^{(1)}\). However, if one approaches this point from an isobaric process or an isovolumetric process, or a more complicated process, we do not know whether such a point exhibits the same singularity. Therefore we must seek for a general condition for critical point, independent of thermodynamic paths.

At the local point of the thermodynamic EoS surface \(p = p(T, V)\), the tangential plane is spanned by two independent vectors \((dT, dV)\). At the critical point \((T_C, V_C)\), we have \((\partial p/\partial V)_T = 0 \quad (1)\) which means existence of a limit along isotherm. Such a limit must exist irrespective along isotherm \((T = \text{const.})\) or along isovolumetric line \((V = \text{const.})\), implying that we can further impose \((\partial p/\partial T)_V = 0\) at the critical point. Another condition is inspired by the Gaussian curvature that is independent of the detailed structure of matter, and the simplest assumption is \(K_C = 0\), implying \(\partial^2 p/\partial V \partial T = 0\). In sum, we propose two additional conditions for the critical point on the EoS surface \(p = p(T, V)\),
\[
(\partial p/\partial T)_V = 0, \quad \partial^2 p/\partial V \partial T = 0.
\]
It is worthy of mentioning that, in contrast to the realistic experiments which seem hard to measure these two response functions near the critical point, the computer simulations are more feasible \(^{(8, 11)}\) which show that the critical slowing down is really an overall phenomenon no matter what path is chosen to approach to the critical point.
III. THE PROPOSAL AND TEMPERATURE DEPENDENCE OF VDW PARAMETERS $a$ and $b$

We are confident that the vdW EoS with constant parameters $a$ and $b$ is not satisfactory for following two senses. The first is that the Gaussian curvature at the critical point is $K_C \approx -0.125$ [13] which is not qualitatively different from other point except the limiting situation. The second is that this value $K_C \approx -0.125$ manifestly depends on special thermodynamic path, i.e., isotherm [1]. Fortunately, the vdW EoS can be adapted for removal of these weaknesses.

The slightest extension of the vdW EoS is to let two constants $a$ and $b$ in the vdW EoS [2] depend on the temperature as $a \rightarrow a(T)$ and $b \rightarrow b(T)$. The critical values of $T_C, V_C, p_C$ are entirely determined by $a(T_C)$ and $b(T_C)$,

$$T_C = \frac{8a(T_C)}{27Rb(T_C)}, p_C = \frac{a(T_C)}{27b(T_C)^2}, V_C = 3b(T_C).$$

With introduction of the dimensionless $\alpha(t^*)$ and $\beta(t^*)$ instead of $a(T)$ and $b(T)$ in the following,

$$\alpha(t^*) \equiv \frac{a(T)}{a(T_C)} = \frac{a(t^*T_C)}{a(T_C)}, \beta(t^*) \equiv \frac{b(T)}{b(T_C)} = \frac{b(t^*T_C)}{b(T_C)},$$

the Law of Corresponding States does not hold true any more except the special case, $\alpha = const.$ and $\beta = const.$, and we have instead the dimensionless extended vdW EoS,

$$p^* = \frac{8}{3} \frac{t^*}{v^* - \beta(t^*)/3} - \frac{3\alpha(t^*)}{v^*^2}.$$

Near the critical point, we assume that $a(T)$ and $b(T)$ parameters take the following forms,

$$a(T) \approx a(T_C) + a'(T_C)(T - T_C) + \frac{1}{2}a''(T_C)^2(T - T_C)^2,$$

$$b(T) \approx b(T_C) + b'(T_C)(T - T_C) + \frac{1}{2}b''(T_C)^2(T - T_C)^2,$$

where,

$$g' = \frac{dg}{dT}, g = a, b, a', b', ....$$

The relations between set $(\alpha'(T_C), \beta'(T_C))$ and set $(a'(T_C), b'(T_C))$ are,

$$\alpha'(t^* = 1) = T_C \frac{a'(T_C)}{a(T_C)}, \beta'(t^* = 1) = T_C \frac{b'(T_C)}{b(T_C)}.$$ 

where $\alpha' = da/dt^*$ and $\beta' = db/dt^*$, etc.

The mean curvature $H$ and Gaussian curvature $K$ of the dimensionless extended vdW EoS surface have very long expressions of complicated structure. However, the expressions for both $H$ and $K$ at the critical point $(t^*, v^*, \alpha, \beta) = (1, 1, 1, 1)$ are simply,

$$H_C = \frac{2\beta' (\beta + 2) - 3\alpha'' + 2\beta''}{2(G(t^*, v^*))^{3/2}}, K_C = -\frac{36(1 - \alpha' + \beta')^2}{(G(t^*, v^*))^2},$$

where,

$$G(t^*, v^*) = 4\beta^2 + 9a^2 - 12a' \beta' + 16 \beta' - 24a' + 17.$$ 

The distinctive feature of the extended vdW EoS is that it contains two possible local shapes at the critical point: hyperbolic and parabolic, for $K_C \leq 0$. The case $K_C = 0$ can be realized provided,

$$1 - \alpha' + \beta' = 0.$$ 

To note that two response functions $(\partial p/\partial T)_V$, and its partial derivative with respect to volume, $(\partial^2 p/\partial V \partial T)$, produce values at the critical point $(T_C, V_C, p_C)$, respectively,

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{9RT_Cb'(T_C) - 4a'(T_C) + 18Rb(T_C)}{36(b(T_C))^2},$$

$$\frac{\partial^2 p}{\partial V \partial T} = -\frac{27RT_Cb'(T_C) - 8a'(T_C) + 27Rb(T_C)}{108(b(T_C))^3}. $$
These two values are sufficient to completely fix two derivatives \((a'(T_C), b'(T_C))\), given that the parameter \(b(T_C)\) in \([21a], [24b]\) is given by the magnitude of the molar critical volume via \([15]\).

Now let us examine situations where both response functions in \([14]\) vanish at the critical point. First, once the second response function vanishes at the critical point, \((\partial^2 p/\partial V \partial T) = 0\), i.e., \(27RT_Cb'(T_C) - 8a'(T_C) + 27Rb(T_C) = 0\) from \([24b]\), we have from the relations \([20]\),

\[
27Rb(T_C)\beta' - 8a' a(T_C) + 27RT_Cb(T_C) = 0.
\]

which reproduces \(1 - \alpha' + \beta' = 0\) \([23]\) with \(27TC Rb(T_C) = 8a(T_C)\) \([15]\). Secondly, once the first response function in \([14]\) vanishes at the critical point, \((\partial p/\partial T)_V = 0\), i.e., \(9RT_Cb'(T_C) - 4a'(T_C) + 18Rb(T_C) = 0\) from \([24a]\), we have \(4 - 3\alpha' + 2\beta' = 0\). An association of two equations \(1 - \alpha' + \beta' = 0\) and \(4 - 3\alpha' + 2\beta' = 0\) yields,

\[
\alpha' = 2, \beta' = 1 \text{i.e., } a'(T_C) = 2a(T_C)/T_C, b'(T_C) = b(T_C)/T_C.
\]

With these values, we find that not only the critical point is locally flat, but also \(a(T)\) and \(b(T)\) are, accurate up to the first order of \((t^*-1)\),

\[
a(T) \approx a(T_C) + 2a(T_C)(t^*-1) = -a(T_C) + 2a(T_C)t^*,
\]

\[
b(T) \approx b(T_C) + b(T_C)(t^*-1) = b(T_C)t^*.
\]

When \(t^* \approx 1\), i.e., \(T \approx T_C\), \(a(T) \approx a(T_C)\) and \(b(T) \approx b(T_C)\), the usual form of vdW EoS is assumed. It is important to note that, from two relations above, the usual vdW EoS is valid when the thermodynamic states are very close to the critical point, and \(a(T)\) and \(b(T)\) are also solely determined by \(a(T_C)\) and \(b(T_C)\).

IV. CONCLUSIONS

Differential geometry is powerful tool to reveal the intrinsic nature of the curved surface, and it is advantageous to analyze the critical point on the EoS surface. On the tangential plane of the critical point, the existence of limit \((\partial p/\partial V)_T = 0\) requires the isothermal process. However, the essence of the critical point is its independence of whatever process is taken, and of detailed structure of matters, etc. We can therefore assume \((\partial p/\partial T)_V = 0\) and \(K_C = 0\) at the critical point on the EoS surface.

The vdW EoS is the simplest one to understand the liquid-gas transition. Since the vdW parameters \(a\) and \(b\) are constant, the Gaussian curvature is negative definite; and there is no distinction between vdW EoS and the ideal gas EoS. According to our assumptions, the vdW EoS is slightly modified or extended such that the vdW parameters \(a\) and \(b\) vary with temperature, allowing for presence of the zero Gaussian curvature at the critical point. Our approach sheds light on understanding the theoretical problem how the vdW parameters depend on the temperature.

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