Phase transition in the high-order nonideal mixing model

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Abstract

We extend the existing second-order nonideal mixing model, which only formally allows for the second-order phase transition, into the fourth-order. The Landau theory reveals that both first- and second-order phase transitions may exist in this higher-order model. Moreover, we show that a single structural parameter determines whether the phase transition abruptly switches between first- and second-orders. We note, it provides an explanation of either appearance or absence of the liquid-liquid critical point in the liquid-liquid phase transition on debate.

In Landau theory [1], the Gibbs free energy $F$ of a system is conventionally expressed as a polynomial expansion of an order parameter $x$. The expansion coefficients vary when temperature $T$ drops. Below a critical value $T_c$, the free energy surface will develop multiple minima which are lower than the energy $F_0$ at $x = 0$, creating various so-called Landau landscapes. If there are two minima (double-well) at $\pm x_0$ with $x_0 \geq 0$, $x_0$ increases above zero continuously with dropping $T$. It gives rise to a second-order spontaneous phase transition. If there are three minima at $\pm x_0$ and $x = 0$ (triple-well), $x_0$ increases above zero only intermittently with dropping $T$. It gives rise to a first-order transition. A recent work [2] has used the Landau theory to study the second-order nonideal mixing among $A$ and $B$, which are the two components or the two states of one component. The Gibbs free energy of such a model has a non-polynomial form,

$$F = G_A(p, T) + yG_{BA}(p, T) + kT(y \ln y + (1 - y)\ln(1 - y)) + \alpha y(1 - y).$$

$y$ is the mole fraction of $B$. $k$ is the Boltzmann constant. $G_A$ is the background free energy. $G_{BA}$ denotes the free energy differences between $A$ and $B$. The third term is due to the ideal mixing entropy. $\alpha y(1 - y)$ is due to the nonideality of mixing. $\alpha$ is assumed to be independent of $T$, which implies that the nonideality contributes to $F$ via enthalpy which stems from the many-body interaction among/between $A$ and $B$ particles. The $n$-body interactions contain only the remaining term which cannot be represented by up to $(n-1)$-body interactions. Therefore, higher-body interactions become smaller than the less-higher-body interactions and are neglected in the second-order nonideality consideration.

Anisimov [2] modeled the fluid polymorphism by tuning both $G_A$ and $G_{BA}$ terms in equation (1) to resolve the divergence of response function of various industrial and academic interesting systems [3]. The polyamorphic solution could not only provide a robust analysis of liquid-liquid transition (LLT) found in the numerical simulation but also interpret experimental observations [4]. It was readily applied to explain a series of works [5–14]. However, as both our study and [2] show, a second-order nonideal mixing model only formally allows for the second-order phase transition. It does not allow for the first-order transition which nonetheless was reported in the literature. For instance, Palmer et al [15] demonstrated the first-order LLT in ST2 water. Meanwhile, most experimental studies indicate that low-density amorphous ice to high-density amorphous ice transition, which shows great analogue to LLT [16], is a sharp first-order phase transition [17–23]. Moreover, Liu et al [24] found evidence of LLT with a liquid-liquid critical point (LLCP) separating the first-order and second-order transitions [25]. But, Chhitelawong et al find that ‘Temperature of Maximum Density’ line is observed in both LLCP and Critical-Point-Free (CPF) scenarios when pressure $P$ is positive. Their studies are new ways to realize the CPF scenario [26]. Apparently, the puzzle of LLCP and CPF demands to be unveiled [27].
In this work, we provide an explanation by extending the second-order nonideal mixing model to include an extra fourth-order nonideality term. We show that, both the first- and second-order phase transitions are now formally allowed. A single structural parameter determines whether the phase transition driven by $T$ abruptly switches between the second- and first-orders. As a result, our theory is compatible with both LLCP and CPF.

We choose $x \equiv y - \frac{1}{2} \in \left[ 1.5, 2 \right]$ as the order parameter because the nonideal mixing should be expanded around the ideal mixing in which $x = 0$ holds. The Landau-relevant terms in equation (1) become

$$f = kT \left[ \frac{1}{2} + x \ln \left( \frac{1}{2} + x \right) + \frac{1}{2} - x \ln \left( \frac{1}{2} - x \right) \right] + \alpha \left( \frac{1}{4} - x^2 \right).$$

We find the turning points, five for the first-order Landau landscape and three for the second-order, by solving

$$f' = \frac{df}{dx} = f'_1 - f'_2 = 0,$$

where $f'_1 \equiv kT \ln \frac{1 + 2x}{1 - 2x}$ and $f'_2 \equiv 2\alpha x$. We focus on the regime of $x \geq 0$ owing to the inversely symmetric expression in equation (3). It is obvious that $x = 0$ is a solution. We insert the Taylor expansion of $f'_1$ into the equation (3) to have

$$(2kT - \alpha)x + kT \sum_{n=2}^{\infty} \frac{(2x)^{2n-1}}{2n - 1} = 0.$$  

Since the two terms are both equal to zero at $x = 0$ and the second term monotonically increases with $x$, a necessary condition for the two terms to be equal again at a nonzero $x$ value is $0 \leq 2kT < \alpha$. To see if this condition is also sufficient, we plot the curve(line) for $f'_1 (f'_2)$ in figure 1(a). We have $f''_1 (x > 0) > f''_2 (x = 0)$ and $f'_2$ is a constant $2\alpha$. For the solid curve of $f'_1$ to cross with the dashed line of $f'_2$ at a nonzero $x$ value, $f''_1 (x = 0) = 4kT < 2\alpha$ must hold. Because $f'_2$ diverges at $x = \frac{1}{2}$, $2kT < \alpha$ is obviously a sufficient condition to have nonzero solutions for equation (4). Therefore, for $0 \leq T < \frac{\alpha}{2kT}$ (Thus, $\alpha > 0$ must hold), there develops a second-order Landau landscape.

The same condition was previously obtained in a different way [2]. We recover it here because the above line of reasoning is used for the richer critical phenomena when we extend equation (1). For the moment, we plot the free energy surfaces for a fixed $\alpha$ value, letting temperature $T$ drop across the critical value $T_c = \frac{\alpha}{2kT}$. For the example shown in figure 1(b), $kT$ decreases from 1.5 to 1.0 every step of 0.1 from bottom to top with $\alpha = 3$. It shows that decrease of temperature does develop the free energy surface into a second-order Landau landscape.

We define $\eta \equiv \frac{kT}{\alpha}$. The continuous emergence of a nonzero order parameter (nonzero solutions of equation (3)) is depicted in figure 1(c). It is consistent with Landau theory that the double-well energy landscape indicates a continuous second-order phase transition.

For the first-order transition to take place, the nonideal mixing model (1) must be extended. Recall that, $\omega_3 (1 - y)$ emerges in equation (1) as a consequence of nonideall mixing and is the only term kept. Necessarily, there are other higher-order terms due to $n$-body interactions. The immediate candidate is the one owing to 3-body interactions, $\omega_1 y (1 - y)^2 + \omega_2 y^2 (1 - y)$. In the case of $\omega_0 \approx \omega_1 \approx \omega$ for fluid polymorphism, it reduces to $\omega \left( \frac{1}{4} - y^2 \right)$. It can be absorbed into the existing terms Thus, the cubic term vanishes. Next, we consider 4-body interactions. They yield an extra term $- \beta_1 y^2 (1-y)^2 - \beta_2 [y (1-y)^2 + y^3 (1-y)]$. It appears as the quadruple term in

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Second-order Landau landscape. (a) The curves (lines) of $f'_1$ ($f'_2$) have steeper slope for larger $2kT$'s ($\alpha$'s). The solid curve and the dashed line need to cross twice, determined by their slope at $x = 0$, in order to yield two nonzero solutions for equation (3). (b) The free energy surface develops a second-order Landau landscape when $T$ drops below $T_c = 1.5kT$ for $\alpha = 3.0$ at the bottom to $1.0kT$ at the top, every segment of $0.1kT$. (c) After $\eta \equiv \frac{kT}{\alpha}$ drops below the critical value $0.30$, a nonzero order parameter $|x_0|$ continuously rises up above zero.}
\end{figure}
with $\beta \equiv \beta_1 + 2\beta_2$. We have neglected a constant in this extra term and absorbed its quadratic contribution into the existing term without loss of generality. Equation (3) becomes

$$ab = \frac{kT}{\ln \frac{x}{1 - 2}} = -0.63$$

We define $f' \equiv 4/\beta x^3$. $f'_3|_{x=0} = 0$ requires

$$2kT > \alpha,$$

for $f' = 0$ to have two nonzero solutions in the interval $0 < x < \frac{1}{2}$. Otherwise, there will exist only one nonzero solution in this interval as stated for the second-order landscape, see figure 1(a). It is worth noting that $2kT < \alpha$ remains as a sufficient condition for there to exist a second-order Landau landscape, only when there is no first-order phase transition prior to it during decrease of temperature. For example, there are still 3 minima even when $kT$ drops below $0.6167$, as shown in figure 2(a), implying that the Landau landscape is not in the second-order even when $2kT < \alpha$ holds in this case.

Thus, there should be another relationship between $\alpha$ and $\beta$. We follow the line of reasoning in equation (4) to have

$$2kT - \alpha)x + \frac{8kT - 6\beta}{3}x^3 + kT \sum_{n=3}^{\infty} \frac{(2x)^{2n-1}}{2n-1} = 0.$$  

Since the coefficients of both the first and third terms are positive, a necessary condition for two nonzero solutions in $(0, \frac{1}{2})$ is

$$\beta > \frac{4kT}{\alpha}.$$  

Combined with the inequality (7), we have

$$\beta > \frac{2\alpha}{3},$$  

as a necessary relationship between $\alpha$ and $\beta$ for the first-order Landau landscape. To see if it is also sufficient, we set the limiting case of $2kT = \alpha$. The first term vanishes. Meanwhile, the last term is in higher orders than the second term and diverges with $x \to \frac{1}{2}$. The following equation

$$\frac{6\beta - 8kT}{3} = kT \sum_{n=3}^{\infty} \frac{2^{2n-1}(x)^{2n-3}}{2n-1}$$

does have solutions in $(0, \frac{1}{2})$ for $\beta > \frac{4kT}{3} = \frac{2\alpha}{3}$. Therefore, condition (10) is sufficient for the first-order Landau landscape. See such an example in figure 2 for $\alpha = 1.0$ and $\beta = 2.5$. (a) Two minima at nonzero $x$ values become lower than the one at $x = 0$ after $kT$ drops below $0.6167\alpha$; (b) $x_0$ changes discontinuously at the critical temperature showing a first-order transition. On the other hand, $2kT < \alpha$ is a sufficient condition for the second-order landscape, actually existing if there is no first-order landscape prior to it or virtually existing otherwise. It implies that, there is a second-order landscape in the extended fourth-order nonideal mixing model with $\beta < \frac{4kT}{3}$. 

Figure 2. First-order Landau landscape for $\alpha = 1.0$ and $\beta = 2.5$. (a) The free energy surface develops a first-order Landau landscape when $kT$ decreases from 0.65 at the bottom to 0.60 at the top, every segment of 0.01. (b) After $\eta = \frac{kT}{\alpha}$ drops below the critical value 0.6167, a nonzero order parameter $x_0$ discontinuously rises above zero.
We explicitly factor out from \( y \Delta B_A \) the difference in one-particle energy \( \gamma_A (\gamma_B) \) of the state/component \( A \) (\( B \)), including vibration and etc. At temperature around \( T_c \), both \( \gamma_A (P, T) \) and \( \gamma_B (P, T) \) are treated as constants.

\[
\gamma_A (T - T_c) y + \gamma_B (T - T_c) (1 - y) \text{ gives a term } (\gamma_A - \gamma_B) T x , \text{ that is bilinear with both order parameter } x \text{ and temperature } T , \text{ and other terms absorbed into the background energy. We then have the fully extended Landau-related free energy expression,}
\]

\[
f = k T \left[ \left( \frac{1}{2} + x \right) \ln \left( \frac{1}{2} + x \right) + \left( \frac{1}{2} - x \right) \ln \left( \frac{1}{2} - x \right) \right] + \alpha \left( \frac{1}{4} - x^2 \right) - \beta x^4 + \gamma T x ,
\]

where \( \gamma = (\gamma_A - \gamma_B) \). Clearly, temperature \( T \) plays a dual-role: to develop Landau landscapes in either first- or second-order, and to trigger the driven phase transitions. See appendix for illustration. We set up two sets of structural parameters in figure 3(a). We fix \( \alpha = 1.0 \) and let \( \beta \) vary around the critical value \( \frac{\alpha}{2} \), above for the first-order Landau landscape and below for the second-order landscape. Naturally, the critical temperature should be close to each other in these two cases. Nevertheless, when we sweep \( T \) around \( T_c \) in both cases, the hysteresis are drastically different, without a loop for the second-order and with an opening loop in the first-order. For the example shown in figure 3(a), we set \( \gamma \) as small as \( 10^{-5} \) to show that even such a small value will make the phase transitions different from those of the conventional Landau theory. In this case, the phase transition is between Phase-1 with zero order parameter and Phase-2 with nonzero order parameter.

Finally, we argue that our model might be able to unveil the puzzle of LLCP and CPF [27]. At higher pressures, the isotherm volume is compressed. It leads to a smaller number of micro-states in the entropy consideration. Thus, the entropy contribution from the nonideal mixing to the free energy is suppressed. In turn, the amplitude of \( \alpha \) in equation (12) decreases, implying that \( T_c \) trends to the low temperature end as \( k T_c \approx \frac{\alpha}{2} \). In the P-T phase diagram, it means that the phase transition line has a negative slope. Meanwhile, at the high temperature end, the particle-particle correlations are weakened. In turn, \( \frac{\alpha}{2} \) decreases. The phase transition line is then divided by a LLCP \( \beta \approx \frac{2 \alpha}{3} \), with the first-order transition at the lower temperature side and the second-order transition at the higher temperature side, see figure 3(b) for schematic. In some fluids or under certain conditions for a fluid, \( \beta \) may always be less or greater than \( \frac{2 \alpha}{3} \). It yields a CPF scenario.

In conclusion, we extended the existing nonideal mixing model by including two extra terms in the Gibbs free energy expression, with the first accounting for the four-body interaction energy in nonideal mixing to give a fourth-order nonideality and the second stemming from difference in one-body energy. We demonstrated that \( T \) plays a dual-role in this extension: to develop richer Landau landscapes with the help from the first extra term; and to linearly couple with the order parameter via the second extra term triggering phase transitions. We show that, while sweeping across \( T_c \) induces phase transition, the order of this transition subjects to an abrupt switch by varying another single structural parameter across its critical value. Our theory provides an explanation of LLT including LLCP alternative to Anisimov’s proposal.

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Appendix. Hysteresis determined by energy landscape

We set larger $\gamma$ values for visual aid of the free energy landscapes in temperature sweeping. (a) $\alpha = 1.0$, $\beta = 3.0$, and $\gamma = 0.03$ for the first-order in figure A1. $kT$ decreases from the right hand side (RHS) to the left hand side (LHS) in the upper row, from 0.800 to 0.575 every augment of $-0.075$. It is followed by the increase of $kT$ from LHS to RHS in the lower row. There is a hysteresis loop. (b) $\alpha = 1.0$, $\beta = 0.5$, and $\gamma = 0.1$ for the second order in figure A1. $kT$ decreases from RHS to LHS in the upper row, from 0.600 to 0.375 every augment of $-0.075$. It is followed by the increase of $kT$ from LHS to RHS in the lower row. Obviously, there is no hysteresis loop in the second-order phase transition while a hysteresis loop opens in the first-order transition. Note that, in these scenarios where $A$ and $B$ states have significant difference in one-particle energy, Phase-1’s order parameter shall have an offset from zero but should be still considered to sit in the ideal mixing value used to expand the nonideal mixing. The critical temperature shall have an offset from $\frac{\Delta}{2k}$ as well.

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Figure A1. Energy landscape determines the hysteresis in temperature sweeping. The system settles (shown as solid circle) in the free energy minima. (a) The first-order. (b) The second-order.