Spinodal curve of a three-component molecular system

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Abstract

We consider a lattice model for three-component systems in which the lattice bonds are covered by molecules of type AA, BB, and AB, and the only interactions are between the molecular ends of a common lattice site. The model is equivalent to the standard Ising model, and the coexistence curves for different lattices and/or some specific form of the interactions have been previously investigated. We derive the spinodal curve of the three-component model on the honeycomb lattice based on the mean-field and Bethe-lattice results of the equivalent Ising model. The spinodal and the coexistence curves of the ternary solution are drawn at different values of the reduced temperature, the only parameter of the model. The particular case of a two-component system is also illustrated.

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1 Introduction

Two almost completely immiscible liquids may increase their mutual solubility in the presence of a solvent. By increasing the solvent concentration, the two liquid layers become more alike and, at some (temperature dependent) composition, a single homogeneous phase is formed. In order to describe this phenomenon, Wheeler and Widom [1] considered three types of diatomic molecules, $AA$, $BB$, and $AB$, covering the bonds of a regular lattice (one molecule per bond) and subject to the condition that only $A$ atoms or only $B$ atoms may meet at a given lattice site (infinite repulsion between $A$ and $B$ atoms of a common site, no interaction otherwise). The model reduces to the standard (spin-1/2, nearest-neighbor interaction) Ising model on the same lattice and its ferromagnetic transition corresponds to a phase-separation transition for the ternary solution. Although the model catches the main aspects of the phase-separation transition, it is not temperature dependent. The model can be extended to include temperature as a significant variable by allowing finite interactions between any two atoms of a common site. This extended Wheeler-Widom model is still equivalent to the standard Ising model but on a decorated lattice in which each site of the original lattice is replaced by a cluster of sites. The exact coexistence (binodal) curves of this extended Wheeler-Widom model on the honeycomb and Bethe lattices were determined in [2] and [3], respectively. Further extensions of the model have been considered in [4, 5, 6].

A solution suddenly quenched from an initial one-phase state in the two-phase region reaches its equilibrium through either a nucleation or a spinodal decomposition process [7]. The states below the coexistence curve can be then classified as metastable (close to the binodal) and unstable (deep in the two-phase region), respectively. The spinodal curve is supposed to separate these two types of behavior. According to the classical (mean-field) theory of first-order phase transitions, the spinodal is defined as the locus for which an appropriate susceptibility diverges; for a multi-component solution, it follows that the determinant of the diffusion coefficients must be zero and this provides an experimental determination of the spinodal curve. Although a mean-field-like approach oversimplifies the problem, it is still a convenient way to distinguish between the metastable and unstable states.

The aim of the present paper is to determine the spinodal curve for the extended Wheeler-Widom model. The molecules are considered to occupy the bonds of a honeycomb lattice (see Fig. 1) and the lattice of the corresponding Ising model is called 3-12 (see Fig. 2). As shown in Section 2, by applying at first a star-triangle transformation and then a double-decoration, the Ising model on the 3-12 lattice becomes the Ising model on the honeycomb
lattice, the original lattice of the molecular model. In Section 3 we shortly review two approximate treatments of the ferromagnetic Ising model: mean-field and Bethe-lattice. The resulting coexistence and spinodal curves for the three-component model, the effect of temperature, and the limit of a two-component system are all presented in Section 4. In the last section we discuss some possible developments of the present work.

2 Extended Wheeler-Widom model on the honeycomb lattice

The grand-canonical partition function of the Wheeler-Widom model with finite interactions on the honeycomb lattice (\( N \) sites) is proportional to the partition function of the standard Ising model on the 3-12 lattice [2]

\[
Z_{3-12} = \sum_{\{\sigma_i\}} \exp \left( R \sum_{(i,j) \subset C_3} \sigma_i \sigma_j + L \sum_{(i,j) \subset C_2} \sigma_i \sigma_j + h \sum \sigma_i \right) \tag{2.1}
\]

with \( \sigma_i, \sigma_j = \pm 1 \) (\( i, j = 1, \ldots, N \)) depending on the spin orientation. The first sum in (2.1) is over all possible configurations, the second one runs over all the triangles (\( C_3 \) graphs) of the 3-12 lattice, the third one is over all the bonds (\( C_2 \) graphs) connecting the triangles, and the last one is over the whole lattice (see Fig. 2). The parameters \( R, L, \) and \( h \) from (2.1) are related to the parameters of the original model as follows

\[
R = \frac{1}{4k_B T} (2\varepsilon_{AB} - \varepsilon_{AA} - \varepsilon_{BB}), \tag{2.2}
\]

\[
L = \frac{1}{4k_B T} (\mu_{AA} + \mu_{BB} - 2\mu_{AB}), \tag{2.3}
\]

and

\[
h = \frac{1}{4k_B T} (\mu_{AA} - \mu_{BB} - 2\varepsilon_{AA} + 2\varepsilon_{BB}). \tag{2.4}
\]

Here \( k_B \) is Boltzmann’s constant and \( T \) is the temperature. We use \( \varepsilon_{AA}, \varepsilon_{AB}, \) and \( \varepsilon_{BB} \) to denote the interaction energies between the molecular ends of a common lattice site. The chemical potentials \( \mu_{AA}, \mu_{BB}, \) and \( \mu_{AB} \) all tend to infinity (no vacant sites are allowed), but differences of any two of them are finite thermodynamic variables.

The partition function of the standard Ising model on the 3-12 lattice can be connected to the partition function of the standard Ising model on the
honeycomb lattice

\[ Z_{\text{hon}} = \sum_{\{\sigma_i\}} \exp \left( K \sum_{<i,j>} \sigma_i \sigma_j + 3h_\ast \sum_i \sigma_i \right) \]  \hspace{1cm} (2.5)

via two transformations: star-triangle followed by double-decoration (see Fig. 3). The result is [8]

\[ Z_{3-12}(R, L, h) = A^{-N}(L_1)B^{3N/2}(L_1, L, h)Z_{\text{hon}}(K, 3h_\ast), \]  \hspace{1cm} (2.6)

where

\[ A^4(L_1) = 16 \cosh(3L_1) \cosh^3(L_1) \]  \hspace{1cm} (2.7)

and

\[ \cosh(2L_1) = \left( e^{4R} + 1 \right) / 2, \quad R > 0, \]  \hspace{1cm} (2.8)

are obtained from the star-triangle transformation, and

\[ B^4 = 16e^{-4L_1} \left[ 1 + e^{2L_1} \cosh(2L_1 + 2h) \right] \left[ 1 + e^{2L_1} \cosh(2L_1 - 2h) \right] \times \left[ \cosh(2L_1) + e^{2L_1} \cosh(2h) \right]^2, \]  \hspace{1cm} (2.9)

\[ e^{4K} = \frac{\left[ 1 + e^{2L_1} \cosh(2L_1 + 2h) \right] \left[ 1 + e^{2L_1} \cosh(2L_1 - 2h) \right]}{\left[ \cosh(2L_1) + e^{2L_1} \cosh(2h) \right]^2}, \]  \hspace{1cm} (2.10)

and

\[ e^{4h_\ast} = \frac{1 + e^{2L_1} \cosh(2L_1 + 2h)}{1 + e^{2L_1} \cosh(2L_1 - 2h)} \]  \hspace{1cm} (2.11)

follow from the double-decoration transformation. The parameter \( L_1 \) from equations (2.6) to (2.11) is an interaction constant of the Ising model on the intermediate lattice (see Fig. 3); its sign is undetermined and, without loss of generality, we may choose \( L_1 > 0 \).

Let us denote by \( X_{AA}, X_{BB}, \) and \( X_{AB} \) the mole fractions respectively corresponding to the three types of the molecules. The mole fractions obey the conservation equation

\[ X_{AA} + X_{BB} + X_{AB} = 1 \]  \hspace{1cm} (2.12)

and they can be related to the quantities of the equivalent Ising model by [2]

\[ X_{AA} + X_{BB} - X_{AB} = \sigma_{3-12} \]  \hspace{1cm} (2.13)

and

\[ X_{AA} - X_{BB} = m_{3-12}, \]  \hspace{1cm} (2.14)
where $\sigma_{3-12} = \langle \sigma_i \sigma_j \rangle_{C_2}$ describes the spin-spin correlation on the $C_2$ graphs and $m_{3-12} = \langle \sigma_i \rangle$ is the magnetization of the 3-12 lattice. Using (2.6), $\sigma_{3-12}$ and $m_{3-12}$ can be expressed in terms of the similar quantities $\sigma$ and $m$ on the honeycomb lattice as

$$\sigma_{3-12} = \left( \frac{\partial \ln B}{\partial L} \right)_{L_1, h} + \left( \frac{\partial K}{\partial L} \right)_{L_1, h} \sigma + 2 \left( \frac{\partial h_*}{\partial L} \right)_{L_1, h} m$$  \hspace{1cm} (2.15)$$

and

$$m_{3-12} = \frac{1}{2} \left( \frac{\partial \ln B}{\partial h} \right)_{L_1, L} + \frac{1}{2} \left( \frac{\partial K}{\partial h} \right)_{L_1, L} \sigma + \left( \frac{\partial h_*}{\partial h} \right)_{L_1, L} m.$$  \hspace{1cm} (2.16)$$

The Ising model has two parameters, $K$ and $h_*$, while the Wheeler-Widom model has three independent combinations of the original parameters: $R$, $L$, and $h$. One can choose $1/R$ as the reduced temperature of the molecular model [2]; we will use $t$ to denote it and keep it constant throughout the calculation. (When $\varepsilon_{AB} \to \infty$, then $t \to 0$ and the model reduces to the original model introduced by Wheeler and Widom [4]; see also Appendix.) Because we describe the molecular model by means of the Ising model, all the derivatives from the equations (2.15) and (2.16) must be expressed in terms of $R$, $K$, and $h_*$ rather than $L_1$, $L$, and $h$. The interaction constant $L_1$ as a function of $R$ is given by (2.8) and from (2.10) and (2.11) we can find $L$ and $h$ as functions of $K$ and $h_*$ at constant $L_1$ (or, equivalently, at constant $t$). Namely,

$$\tanh(2h) = \frac{\sinh(2L_1) \sinh(2h_*)}{\cosh(2L_1) \cosh(2h_*) - e^{-2R}} \equiv \chi$$  \hspace{1cm} (2.17)$$

and

$$\frac{e^{2L}}{\sqrt{1 - \chi^2}} = \frac{\cosh(2L_1) \cosh(2h_*) - e^{-2K}}{\cosh(2L_1) e^{-2K} - \cosh(2h_*)} \equiv \lambda.$$  \hspace{1cm} (2.18)$$

The expressions (2.17) and (2.18) are well defined only if $|\chi| < 1$ and $\lambda > 0$, which amounts to

$$|h_*| < L_1$$  \hspace{1cm} (2.19)$$

and

$$-\frac{1}{2} \ln[\cosh(2L_1 - 2|h_*|)] < K < \frac{1}{2} \ln \left[ \frac{\cosh(2L_1)}{\cosh(2h_*)} \right] \equiv K_{\text{max}},$$  \hspace{1cm} (2.20)$$

the latter inequalities determining the region in the $(K, h_*)$-space which can be mapped into $(L, h; R)$-space. This region becomes the whole space when
$R \to \infty$. The derivatives from (2.15) and (2.16) as functions of $K$, $h_\star$, and $R$ are given in Appendix. Provided $\sigma$ and $m$ (both functions of $K$ and $h_\star$) are known, we have now the complete “dictionary” between our molecular system and the Ising model.

The ferromagnetic transition of the Ising model ($K > K_c > 0$, $h_\star = 0$) corresponds to a phase-separation transition for the Wheeler-Widom model ($L > 0$, $h = 0$). If $\sigma_0(K) \equiv \sigma(K, 0)$ and the spontaneous magnetization $m_0(K) \equiv m(K, 0)$ from (2.13) and (2.14) are specified, then one can determine the isothermal coexistence curves for our molecular system by eliminating $K$ between the equations (2.13) and (2.14). The coexistence curves based on the exact solution of the Ising model on the honeycomb lattice and on the three-coordinated Bethe lattice were determined in the [2] and [3], respectively. In finding the spinodal curve, we need $\sigma_\star(K) \equiv \sigma[K, h^{(s)}_\star(K)]$ and $m_\star(K) \equiv m[K, h^{(s)}_\star(K)]$ calculated along a certain path $h^{(s)}_\star(K)$ of the Ising model. We consider two approximate methods below: mean-field and Bethe-lattice.

3 Ising ferromagnet in the mean-field approximation and on the Bethe lattice

In the mean-field approximation, the magnetization of the Ising model with the partition function (2.5) is the solution of the equation [4]

$$m = \tanh(qKm + 3h_\star),$$

(3.1)

where $q$ is the coordination number of the lattice. This equation is invariant under the transformation $(m, h_\star) \to (-m, -h_\star)$, i.e., $h_\star$ is an odd function of $m$. The spin-spin correlation function $\sigma$ can be determined, for example, by using its relation to the internal energy per spin $u$,

$$\sigma = \frac{2}{qK} \left( \frac{u}{k_BT} + 3h_\star m \right),$$

(3.2)

and substituting the expression for $u$ from [4] into (3.2). As a result,

$$\sigma = m^2.$$  

(3.3)

In zero magnetic field and for $K > K_c = 1/q$ the model exhibits a ferromagnetic transition. The spontaneous magnetization is given by (3.1) with $h_\star = 0$: if $m_0$ is a solution, then $-m_0$ is also a solution and both these values minimize the free energy as function of the magnetization. Once
having determined the spontaneous magnetization, the relation (3.3) gives $\sigma_0 = m_0^2$. At constant $K$, the “van der Waals loops” of $h_\ast$ as function of $m$ (for $|m| < |m_0|$) are interpreted within mean-field-like theories as non-equilibrium states: metastable for $|m| > |m_s|$ and unstable for $|m| < |m_s|$, where $\pm m_s$ give the extremum points of $h_\ast$ (which, at the same time, are the inflexion points of the free energy as a function of the magnetization). By changing $K$, these two extremum points describe the spinodal curve, and the mean-field value of $m_s$ is

$$m_s = \pm \sqrt{1 - \frac{K_c}{K}} \text{ with } K_c = \frac{1}{q}. \quad (3.4)$$

The spin-spin correlation function along the spinodal curve is then given by $\sigma_s = m_s^2$.

In an improved scheme, with the same results as the Bethe approximation [10], we consider the Ising model on the Bethe lattice (see Fig. 4). Defining

$$z = e^{-2K}, \mu = e^{-6h_\ast}, \text{ and } \mu_1 = \mu x^{q-1}, \quad (3.5)$$

the magnetization of the Ising model on the Bethe lattice with the coordination number $q$ is [10]

$$m = \frac{1 - \mu_1^2}{1 + 2z\mu_1 + \mu_1^2}, \quad (3.6)$$

while the spin-spin correlation function is [11]

$$\sigma = \frac{1 - 2z\mu_1 + \mu_1^2}{1 + 2z\mu_1 + \mu_1^2}, \quad (3.7)$$

where $\mu_1$ obeys the equation

$$\frac{\mu_1}{\mu} = \left(\frac{z + \mu_1}{1 + z\mu_1}\right)^{q-1}. \quad (3.8)$$

From (3.6) and (3.7) we can get $\sigma$ as a function of $z$ and $m$,

$$\sigma = 1 - 2z \frac{1 - m^2}{z + \sqrt{1 - (1 - z^2)m^2}}. \quad (3.9)$$

This is the analog of Eq. (3.3) of the mean-field approximation and, for $z \to 1$ ($K \to 0$, i.e., small couplings), they coincide. In zero magnetic field and for $z < z_c = 1 - 2/q$ the model undergoes a ferromagnetic transition. Both $m_0$ and $\sigma_0$ can be determined in principle by solving at first (3.8) with
\[ \mu = 1 \] and then substituting the solution \( \mu_1(z) \) into (3.6) and (3.7). In the particular case of \( q = 3 \) one gets

\[
m_0 = \pm \frac{1}{2z} \left( \frac{1 - 3z}{1 + z} \right)^{1/2}
\]

and

\[
\sigma_0 = 1 + 2z \left[ \frac{1}{1 - z} - \frac{1}{3(1 + z)} - \frac{2}{3(1 - 2z)} \right].
\]

In determining the spinodal curve, we should first derive \( \mu \) as a function of \( m \) using (3.6) and (3.8), and then one readily shows that \( h_\star \) has extrema points at

\[
m_s = \pm \sqrt{\frac{1 - z^2 / z_c^2}{1 - z^2}} \quad \text{with} \quad z_c = 1 - \frac{2}{q}.
\]

Combining (3.12) with (3.9) we easily find \( \sigma_s \).

## 4 Phase diagrams

The ferromagnetic transition of the Ising model occurs in zero magnetic field and for a coupling constant \( K \) greater than a critical one \( K_c \). This transition has a correspondent in the molecular model only if \( K_{\text{max}} \) from (2.20), calculated at \( h_\star = 0 \), is greater than \( K_c \). The condition \( \ln[\cosh(2L_1)] = 2K_c \) then determines the **upper consolute temperature** \( t_u \) of the model, i.e., the maximum temperature at which a phase separation transition can occur in the solution,

\[
t_u = \frac{4}{\ln[2e^{2K_c} - 1]}.
\]

In the mean-field approximation of the Ising model \((q = 3)\) we get \( t_u \simeq 3.762 \); for the Bethe lattice, one has \( t_u = 4/\ln 5 \simeq 2.485 \).

In drawing the isothermal coexistence and spinodal curves, we use the triangular diagram: a fixed composition is represented by a point inside an equilateral triangle of the unit height, the mole fraction of each component being given by the distance from that point to the corresponding side of the triangle. For a triangular diagram, the conservation equation (2.12) is automatically fulfilled, and the correspondence with the three components of the molecular solution is chosen as shown in Fig. 5.

Both the coexistence and the spinodal curves are symmetric under reflections around the \((X_{AA} = X_{BB})\)-axis, a consequence of the symmetry properties of the derivatives from (2.13) and (2.14) when \( h_\star \to -h_\star \) (see Appendix).
The analog of the Curie point for a ferromagnet is the \textit{plait point}; it is given by the limit $K \to K_c$ and it lies always on the $(X_{AA} = X_{BB})$-axis. At the plait point, the spinodal curve is tangent to the coexistence curve. In the vicinity of the plait point, both the coexistence and the spinodal curves can be approximated by parabolas. In the opposite limit, at $K = K_{\text{max}}$, it is shown in Appendix that $X_{AB} = 0$ and, thus, both the coexistence and spinodal curves reach the base of the triangular diagram.

The phase diagrams at some particular values of the reduced temperatures are presented in Figs. 5 and 6, respectively corresponding to the mean-field and Bethe-lattice approximations of the equivalent Ising model. In the mean-field approximation (Fig. 5), at $t = 0$ the spinodal and the coexistence curve coincide; they are described by the same parabola $y = (1 - 3x^2)/2$. This means that no metastable states are predicted at zero temperature, an expected result from more general considerations. Technically, this is a consequence of the relation (3.3) between $\sigma$ and $m$, which is independent of the coupling constant $K$: the distinct $K$-dependencies of $m$ for the spinodal and coexistence curves play only a scaling role (the same curve is covered in different ways). In the Bethe-lattice case (Fig. 6), the relation (3.9) between $\sigma$ and $m$ explicitly depends on the coupling constant, and, in general, it should be so. Consequently, the three-component system can be in a metastable state even at zero temperature, a fact that might reveal an inconsistency of the theory. (The implications of this result and a possible way to overcome the difficulty within mean-field-like theories of first-order phase transitions will be discussed in a forthcoming paper.) By increasing the temperature, the curves go down and shrink to a point when $t = t_u$. The limiting case $X_{AB} = 0$ corresponds to a two-component system. In the mean-field approximation of the equivalent Ising model, the spinodal and the coexistence curves depend on temperature as in Fig. 7; the case of the Bethe lattice is illustrated in Fig. 8.

5 Discussion

The Wheeler-Widom model (with finite, two-body interactions) for three-component molecular systems is equivalent to the standard (spin-1/2, nearest-neighbor interaction) Ising model. Based on this equivalence, we derived the spinodal curve for the molecular model on a honeycomb lattice using approximate (mean-field and Bethe-lattice) results for the Ising model. Both the spinodal and the (previously determined) coexistence curves have been drawn at different temperatures.

The present work can be extended in several ways. One direction is
to consider \textit{three-body} interactions between the molecular ends associated with the same site of the honeycomb lattice. The coexistence curves then become \textit{asymmetric}, with the plait point located off the \((X_{AA} = X_{BB})\)-axis of the triangular diagram \([3]\); a similar asymmetry should be observed for the corresponding spinodal curves. Another possible development is to determine the spinodals for systems with both upper and \textit{lower} consolute temperatures. Within the present formalism, a lower bound on the transition temperature follows from the assumption that the molecular ends may form \textit{bonds}; the coexistence surface for a three-coordinate Bethe lattice has been determined in \([4]\). A more general situation, with two possible transitions (one with both upper and lower consolute temperatures, the second one only with an upper consolute temperature below the minimum transition temperature of the first one) has been analyzed in \([3]\). It is also possible to generate phase diagrams with all the characteristics mentioned above (asymmetric, upper and lower consolute temperatures, etc.) within a single ternary solution model of the Wheeler-Widom type \([12]\).

In the framework of the formalism presented above, the spinodal curve of a ternary solution is determined starting from a simple microscopic model reducible to two components. Together with analysis of experimental data, it could contribute to a better understanding of interesting phenomena such as diffusion and nucleation in multi-component systems. Another important aspect should also be mentioned: since a Wheeler-Widom-type model is equivalent to the standard Ising model, it perhaps provides the only way to get exact results for systems with three components.

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Appendix

Let us denote the derivatives that appear in (2.15) and (2.16) by

\[
\begin{align*}
\frac{c_{11}}{c_{12}} & = \left( \frac{\partial \ln B}{\partial L} \right)_{L_1, h}, \quad \frac{c_{21}}{c_{22}} = \frac{1}{2} \left( \frac{\partial \ln B}{\partial h} \right)_{L_1, L}, \\
\frac{c_{13}}{c_{12}} & = \left( \frac{\partial K}{\partial L} \right)_{L_1, h}, \quad \frac{c_{23}}{c_{22}} = \left( \frac{\partial K}{\partial h} \right)_{L_1, L}.
\end{align*}
\] (A.1)

Using the notations

\[
p = \left( e^{4R} + 1 \right) / 2 \quad \text{and} \quad z = e^{-2K},
\] (A.2)

the quantities \( \chi \) and \( \lambda \) respectively defined in (2.17) and (2.18) become

\[
\chi = \frac{\sqrt{p^2 - 1}}{p} \sinh(2h_*) \quad \text{and} \quad \lambda = \frac{p \cosh(2h_*) - z}{pz - \cosh(2h_*)}.
\] (A.3)

Introducing

\[
\omega = (1 + p\lambda)^2 - (p^2 - 1)\chi^2\lambda^2,
\] (A.4)

the \( c \)-quantities from (A.1) are given in terms of \( K \), \( h_* \), and \( R \) as

\[
\begin{align*}
\frac{c_{11}}{c_{12}} & = \frac{\lambda}{p + \lambda} - \frac{1 + p\lambda}{\omega}, \quad \frac{c_{21}}{c_{22}} = \frac{1 + z^2}{2} \frac{\chi\lambda}{p + \lambda}, \\
\frac{c_{13}}{c_{12}} & = \frac{p}{p + \lambda} - \frac{1 + p\lambda}{\omega}, \quad \frac{c_{23}}{c_{22}} = -\frac{1 - z^2}{2} \frac{\chi\lambda}{p + \lambda},
\end{align*}
\] (A.5)

Taking the limit \( R \to \infty \) in (A.3), we get \( c_{11} = c_{13} = c_{21} = c_{22} = 0 \) and \( c_{12} = c_{23} = 1 \). This limit, understood as \( \varepsilon_{AB} \to \infty \) [see (2.2)], corresponds to the original model introduced by Wheeler and Widom [1].

Let us remark that \( \chi \) is an odd function of \( h_* \), while \( \lambda \) and \( \omega \) are even functions of \( h_* \) [see (A.3) and (A.4)]. As a consequence, the quantities \( c_{11} \), \( c_{12} \), and \( c_{23} \) are symmetric under the transformation \( h_* \to -h_* \), whereas \( c_{13} \), \( c_{21} \), and \( c_{22} \) are antisymmetric. Because \( m \) is antisymmetric in \( h_* \) and \( \sigma \)
is an even function of $m$ (see Section 3), from the mole fractions equations (2.12) to (2.14) it follows that $X_{AB}$ is symmetric in $h_*$, while $X_{AA} - X_{BB}$ is antisymmetric. These properties determine the symmetry of the phase diagrams (discussed in Section 4) under reflections around the $(X_{AA} = X_{BB})$-axis. Moreover, at $h_* = 0$ all $c_{13} = c_{21} = c_{22} = 0$ and $\sigma_{3,12}$ decouples from $m_{3,12}$ [see (2.15) and (2.16)].

Another interesting limit is when $K \to K_{\text{max}}$ [see (2.20)]. In this case $\lambda \to \infty$, $\omega$ goes to infinity as $\lambda^2$, and from (A.3) we get $c_{11} = 1$, $c_{12} = c_{13} = 0$; consequently, $\sigma_{3,12}$ given by (2.15) is equal to one. From (2.12) and (2.13) it then follows that $X_{AB} = 0$. This property is used in Section 4 to show that in the limit $K \to K_{\text{max}}$ the coexistence and the spinodal curves always reach the bottom side of the triangular diagram.

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Figure 1: Configuration of molecules within the extended Wheeler-Widom model on the honeycomb lattice.
Figure 2: A portion of the 3-12 lattice, each site being covered by one $C_3$ graph (triangle) and one $C_2$ graph (segment connecting two triangles).
Figure 3: Star-triangle transformation (up) and double-decoration (down) by which the Ising model on the 3-12 lattice can be transformed into the Ising model on the honeycomb lattice. At constant $L_1$, the double-decoration can be also inverted (i.e., from right to left).
Figure 4: The Cayley tree with the coordination number $q = 3$ and the number of shells $n = 4$. The Bethe lattice corresponds to the limit $n \to \infty$. 
Figure 5: Isothermal phase diagrams of the extended Wheeler-Widom model on the honeycomb lattice when the equivalent Ising model is treated in the mean-field approximation (\( t \) is the reduced temperature of the model). The coexistence curves are drawn by solid lines, while the spinodal curves by dashed lines; the solid circles mark the corresponding plait points. At \( t = 0 \) the two curves (coexistence and spinodal) coincide.
Figure 6: The same as in Fig. 5, but in the Bethe-lattice case. At $t = 0$ the spinodal curve does not coincide with the coexistence curve.
Figure 7: The phase diagram of the extended Wheeler-Widom model on the honeycomb lattice in the limit of two components ($X_{AB} = 0$) and when the equivalent Ising model is treated in the mean-field approximation. The coexistence curve is represented by a solid line, the spinodal by a dashed line, and the plait point by a solid circle.
Figure 8: The same as in Fig. 7, but in the Bethe-lattice case.