Exact results for a model ternary solution with strong three-body interactions

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Abstract

We consider a lattice model for three-component systems in which the lattice (honeycomb or three-coordinated Bethe) 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 reduces to a standard Ising model on the original honeycomb or Bethe lattice and the exact coexistence curves for phase separation have been previously calculated for weak three-body interactions. In the present paper we analyze by the same technique the case of strong three-body interactions, the difference being that now the Ising parameters on the intermediate lattice are complex. Exact, closed-form expressions are obtained for the two-phase coexistence surface in temperature-composition space. The exact coexistence curves are drawn for various values of a reduced three-body coupling constant and the reduced temperature. We show there is no phase separation in the model on the considered lattices for sufficiently large three-body coupling constant.

1 Introduction

The main aspects of liquid-liquid equilibria in three-component solutions can be described within a simple lattice model introduced by Wheeler and Widom [1]: each bond of a regular lattice is covered by one rodlike molecule of type AA, BB, or AB, with the condition that only molecular ends (A or B) of the same type may meet at any lattice site. The model reduces to the standard spin-1/2 Ising model with nearest-neighbor interactions on the same lattice, its ferromagnetic transition corresponding to a phase-separation transition for the ternary solution. The original model has been extended to include temperature effects by allowing finite interactions between any two atoms near a common site [2], in which case the model becomes equivalent to the standard Ising model but on an associated lattice.

A further extension of the model was introduced by Strout, Huckaby, and Wu [3], who assumed *three-body* interactions between the atoms near a common site of the honeycomb or three-coordinated Bethe lattice (see Fig. 1). In this case, the molecular model is equivalent to the Ising model on an associated lattice (see Fig. 2) with both two-body interactions (coupling constants R and L) and three-body interactions (coupling constant R_3). The Ising model on the associated lattice can be transformed via a star-triangle transformation to an Ising model on an intermediate lattice, then via a double-decoration transformation to an Ising model on the original honeycomb or Bethe lattice. These transformations are valid for all values of the parameter $\alpha_3 \equiv R_3/R$. Examples of the case $|\alpha_3| < 1$ were considered in [3], and in that case the parameters on the intermediate lattice are all real. In the present paper we use appropriate complex values for the parameters on the intermediate lattice to obtain numerical solutions for the case $|\alpha_3| \geq 1$. Moreover, for the case of strong three-body interactions we obtain the interesting result that there is no phase separation in the ternary solution model on the honeycomb lattice if $|\alpha_3| > 3$ and on the Bethe lattice if $|\alpha_3| > 5$.

2 Ising representation of the model

The partition function of the ternary solution model on the honeycomb or three-coordinated Bethe lattice with N_t vertices (Fig. 1) is proportional to the partition function of the Ising model on a decorated lattice (Fig. 2) [3]

$$Z_{\text{decor}} = \sum_{\{\sigma_i\}} \exp \left(R_3 \sum_{(i,j,k)\subset C_3} \sigma_i\sigma_j\sigma_k + R \sum_{(i,j)\subset C_3} \sigma_i\sigma_j \right.$$

$$+L\sum_{(i,j)\subset C_2}\sigma_i\sigma_j+h\sum_i\sigma_i\Bigg) \tag{1}$$

where C_3 and C_2 denote the triangles of the decorated lattice and the bonds connecting the triangles, respectively. The parameters from (1) are expressed in terms of the interaction energies between the molecules, chemical potentials, and temperature, through the relationships [3]

$$R_3 = \frac{1}{8kT}(3\varepsilon_{ABA}-3\varepsilon_{BAB}-\varepsilon_{AAA}+\varepsilon_{BBB}) \tag{2}$$

$$R = \frac{1}{8kT}(\varepsilon_{ABA}+\varepsilon_{BAB}-\varepsilon_{AAA}-\varepsilon_{BBB}) \tag{3}$$

$$L = \frac{1}{4kT}(\mu_{AA}+\mu_{BB}-2\mu_{AB}), \tag{4}$$

$$h = \frac{1}{4kT}\left[\mu_{AA}-\mu_{BB}+\frac{1}{2}(\varepsilon_{BAB}-\varepsilon_{ABA}+\varepsilon_{BBB}-\varepsilon_{AAA})\right] \tag{5}$$

The partition function of (1) can be related to the partition function of the standard Ising model on the honeycomb or Bethe lattice

$$Z=\sum_{\{\sigma_i\}}\exp\left(K\sum_{<i,j>}\sigma_i\sigma_j+H\sum_i\sigma_i\right) \tag{6}$$

via two transformations (see Fig. 3): a *star-triangle*

$$A^8=2^8\cosh(3L_1+h_1)\cosh(3L_1-h_1)\cosh^3(L_1+h_1)\cosh^3(L_1-h_1), \tag{7}$$

$$\cosh^2(2L_1) = \frac{\left(e^{4R}+1\right)^2}{4\left[1-\sinh^2(2R_3)/\sinh^2(2R)\right]}, \tag{8}$$

$$\cosh(2h_1) = \frac{4\cosh^2(2L_1)-e^{8R}-3}{e^{8R}-1}\cosh(2L_1), \tag{9}$$

$$e^{8h_2} = \frac{\cosh(3L_1-h_1)\cosh(L_1-h_1)}{\cosh(3L_1+h_1)\cosh(L_1+h_1)}e^{8h}, \tag{10}$$

followed by a *double-decoration*

$$\begin{aligned} B^4 &= 2^4e^{4L}\left[\cosh(2L_1+2h_2)+e^{-2L}\right]\left[\cosh(2L_1-2h_2)+e^{-2L}\right] \\ &\times\left[\cosh(2h_2)+e^{-2L}\cosh(2L_1)\right]^2, \end{aligned} \tag{11}$$

$$e^{4K} = \frac{\left[\cosh(2L_1+2h_2)+e^{-2L}\right]\left[\cosh(2L_1-2h_2)+e^{-2L}\right]}{\left[\cosh(2h_2)+e^{-2L}\cosh(2L_1)\right]^2}, \tag{12}$$

$$e^{4H/3} = \frac{\cosh(2L_1+2h_2)+e^{-2L}}{\cosh(2L_1-2h_2)+e^{-2L}}\, e^{4h_1/3}. \tag{13}$$

The relation between the two partition functions is

$$Z_{\text{decor}}(L,h;R_3,R) = A^{-N_t}(L_1,h_1)B^{3N_t/2}(L,h_2;L_1)Z(K,H). \tag{14}$$

The mole fractions of the ternary solution are related to the quantities of the equivalent Ising model by

$$X_{AA}+X_{BB}+X_{AB} = 1, \tag{15}$$

$$X_{AA}+X_{BB}-X_{AB} = \sigma_{\text{decor}}, \tag{16}$$

$$X_{AA}-X_{BB} = m_{\text{decor}}, \tag{17}$$

where the spin-spin correlation function σ_{decor} and the magnetization m_{decor} of the Ising model on the decorated lattice are expressed in terms of the similar quantities on the original (honeycomb or Bethe) lattice through [3]

$$\sigma_{\text{decor}} = \left(\frac{\partial \ln B}{\partial L}\right)_{L_1,h_2} + \left(\frac{\partial K}{\partial L}\right)_{L_1,h_2}\sigma + \frac{2}{3}\left(\frac{\partial H}{\partial L}\right)_{L_1,h_1,h_2} m \tag{18}$$

$$m_{\text{decor}} = \frac{1}{2}\left[\left(\frac{\partial \ln B}{\partial h_2}\right)_{L,L_1} + \left(\frac{\partial K}{\partial h_2}\right)_{L,L_1}\sigma + \frac{2}{3}\left(\frac{\partial H}{\partial h_2}\right)_{L,L_1,h_1} m\right] \times \left(\frac{\partial h_2}{\partial h}\right)_{R_3,R}. \tag{19}$$

σ and m are both functions of K and H, and, because we want to describe the molecular model by means of the Ising model, all the derivatives from (18) and (19) must be expressed in terms of the same quantities and the model parameters R_3 and R; this can be done as explained in [4].

As long as $|R_3| < R$, the quantities L_1, h_1, and h_2 determined from (8)–(10) can be chosen real numbers; this case was considered in [3]. However, for $|R_3| > R$, from (8) it follows that $\cosh(2L_1)$ becomes imaginary and consequently, $\cosh(2h_1)$ given by (9) becomes also an imaginary quantity. We may allow complex values for L_1, h_1, and h_2 on the intermediate lattice, as long as all the quantities on the initial and final lattices are real. Requiring that the real parts of L_1, h_1, and h_2 have at $|R_3| = R$ the same left and right (infinite) limits, one can prove that for $|R_3| > R$ we can choose

$$L_1 = L_1' + i\,\frac{\pi}{4}, \quad L_1' > 0, \tag{20}$$

$$h_1 = h_1' + i\ \mathrm{sgn}(h_1')\frac{3\pi}{4}, \quad \mathrm{sgn}(h_1') = -\mathrm{sgn}(R_3), \tag{21}$$

$$h_2 = h_2' + i\ \mathrm{sgn}(h_2')\frac{\pi}{4}, \tag{22}$$

where the real parts L_1', h_1', and h_2' are uniquely determined in terms of R_3, R, and h by Eqs. (8)–(10).

Since the ferromagnetic transition of the Ising model occurs at $H = 0$ (and $K > 0$), then, to calculate the coexistence curve for the molecular model (at fixed $\alpha_3 \equiv R_3/R$ and the reduced temperature $T' \equiv 1/R$) we need only the zero field values of σ and m. These values are known exactly for both honeycomb and three-coordinated Bethe lattices and can be taken, for example, from Ref. [4]; the derivatives from (18) and (19), at $H = 0$ and for arbitrary R_3 and R, are given in the Appendix of the same reference as exact closed-form expressions in terms of the single parameter $z = \exp(-2K)$. Using Eqs. (15)–(17), the quantities X_{AA}, X_{BB}, and X_{AB} can be calculated at constant R_3 and R for possible values of K, this generating the coexistence curve at constant α_3 and T'. The plait point corresponds to $z = z_c$, where $z_c = 2 - \sqrt{3}$ for the honeycomb lattice and $z_c = 1/3$ for the Bethe lattice.

3 Phase diagrams

The existence of a phase transition for the Ising model on the honeycomb or Bethe lattice is restricted to the conditions $H = 0$ and $z \le z_c$. However, there is another restriction for z which comes from the validity of the double-decoration transformation [4]. In the (α_3, T')-space, a phase transition may occur only below the corresponding curve represented in Fig. 4; the maximum value of $|\alpha_3|$ at which this happens is 3 for the honeycomb lattice and 5 for the Bethe lattice. In the particular case of $\alpha_3 = 0$, we obtain the same maximum values of T' allowing a phase transition as in previous works: $4/\ln(3 + 2\sqrt{3}) \simeq 2.143$ for the honeycomb lattice [2], and $4/\ln 5 \simeq 2.485$ for the three-coordinated Bethe lattice [5].

We draw the phase diagrams for the ternary solution model in a triangular coordinate system, in which case the conservation equation (15) is automatically fulfilled. The phase diagrams are symmetric under the transformation

$\{\alpha_3 \to -\alpha_3,\ X_{AA} \to X_{BB},\ X_{BB} \to X_{AA}\}$. Consequently, we consider only positive values of α_3. The coexistence curves for $\alpha_3 = 1$ ($R_3 = R$), at three different values of the reduced temperature, are represented in Fig. 5 for both the honeycomb and Bethe lattices. At $T' = 0$, the coexistence curve is symmetric around the ($X_{AA} = X_{BB}$)-axis. By increasing the temperature, the coexistence curve becomes asymmetric, flatter, and finally shrinks to a point at a certain value of T'. The same effect of temperature has been determined in the weak three-body coupling regime [3], and it can be remarked also for larger values of α_3. Something similar happens by increasing the value of α_3 at constant temperature, as one can see in Fig. 6 for $T' = 1.5$. It follows that R_3 and R in (1) are competitive: increasing R favors the occurrence of an ordered state (phase-separation), and increasing R_3 acts against this process.

The particular case of a two-component system ($X_{AB} = 0$) is illustrated in Fig. 7. By increasing α_3, the coexistence curve becomes flatter and more asymmetric, until it degenerates in a horizontal line at the maximum critical value of α_3. However, there are some differences between the two lattices: (i) for the honeycomb lattice, the final plait point (at $T' = 0$) corresponds to $X_{AA} \simeq 0.693$, while for the Bethe lattice, $X_{AA} = 1$; (ii) by approaching the maximum critical value of α_3, the asymmetry of the coexistence curve is more pronounced in the Bethe lattice case, where the occurrence of a double inflexion can be remarked.

Acknowledgments

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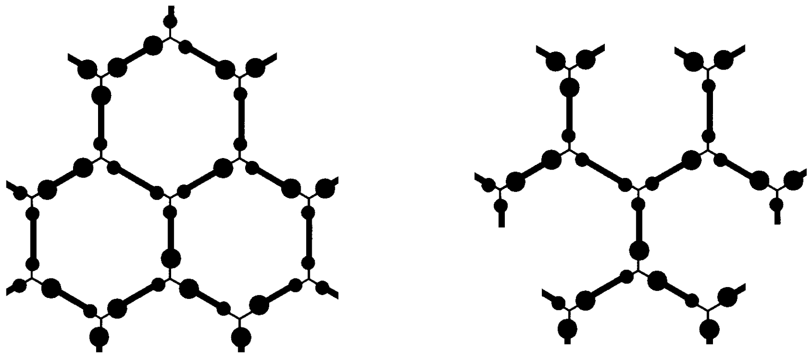

Figure 1: Configuration of molecules on the honeycomb and Bethe lattices. Molecular ends of types A and B are depicted by disks of two different sizes.

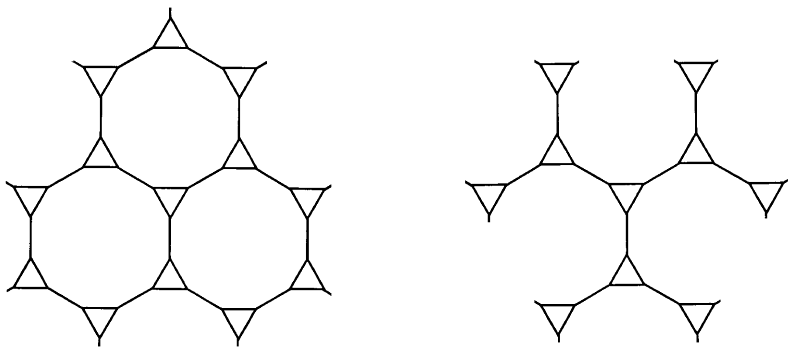

Figure 2: Lattices associated with the model on the honeycomb and Bethe lattices.

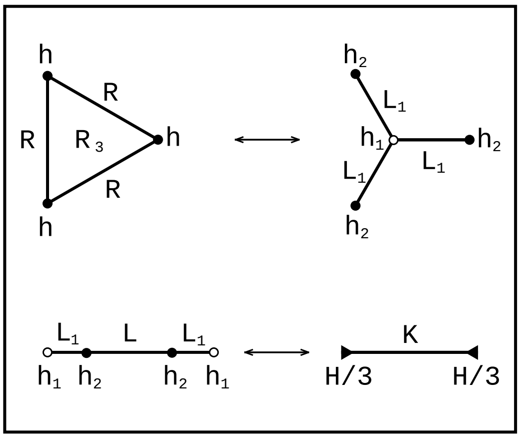

Figure 3: The star-triangle and double-decoration transformations, by which the Ising model on a lattice from Fig. 2 can be transformed into the Ising model on the honeycomb or Bethe lattice.

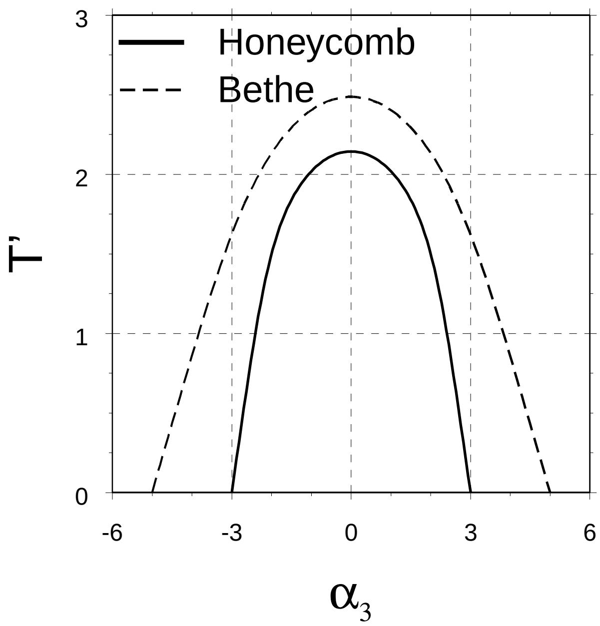

Figure 4: A ferromagnetic transition for the Ising model with the partition function (1) occurs only below the curve corresponding to one of the two considered lattices. ($\alpha_3 \equiv R_3/R$, $T' \equiv 1/R$.)

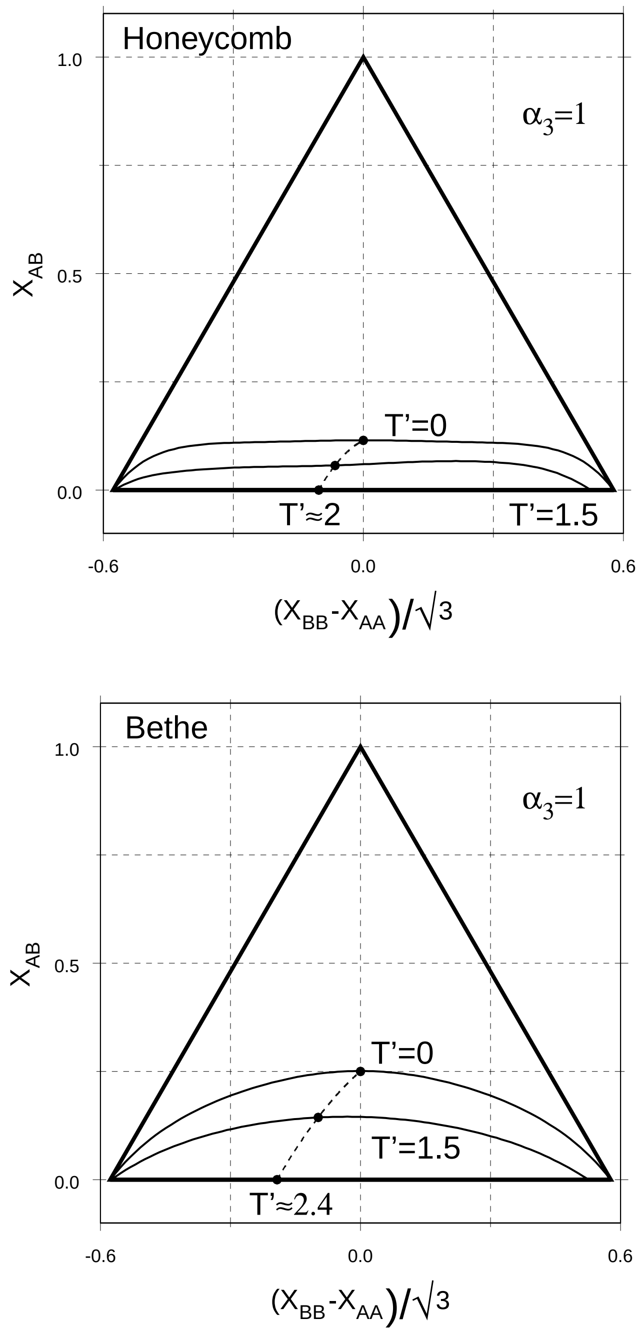

Figure 5: The exact coexistence curves of the ternary solution model at $\alpha_3 = 1$ and various temperatures. A solid circle indicates the position of the plait point, and the dashed line shows how the plait point moves by changing the temperature.

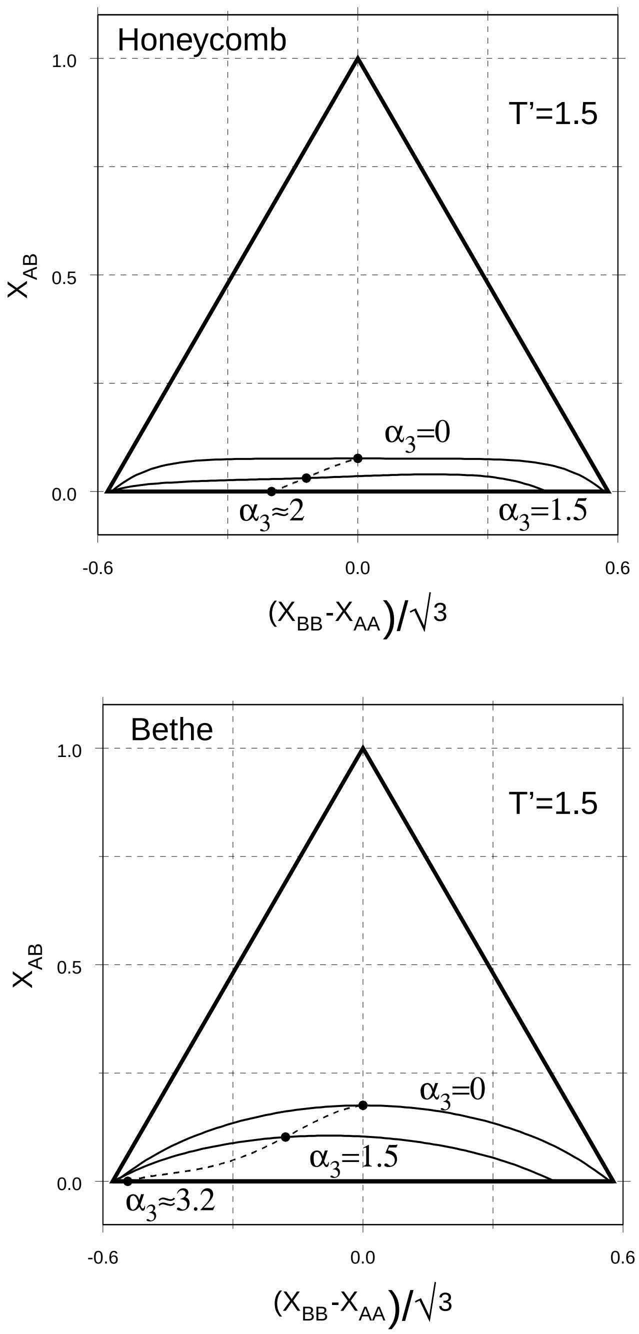

Figure 6: The same as in Fig. 5, but for $T' = 1.5$ and different α_3 values.

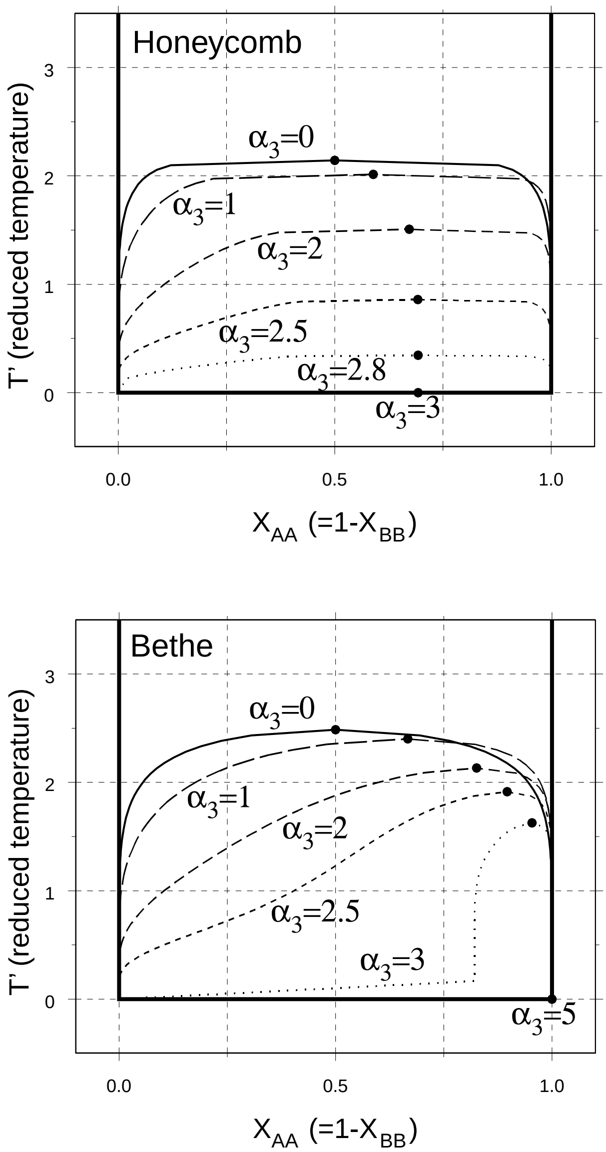

Figure 7: The exact coexistence curves at different α_3 values, in the particular case of a binary solution ($X_{AB} = 0$).