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The two-dimensional alternative binary L-J system: liquid–gas phase diagram

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A two-dimensional (2D) binary system without considering the Lennard-Jones (L-J) potential has been studied by using the Collins model. In this paper, we introduce the L-J potential into the 2D binary system and consider the existence of the holes that are called the "molecular fraction". The liquid–gas phase diagram of the 2D alternative binary L-J system is obtained. The results are quite analogous to the behaviour of 3D substances.

Keywords: L-J potential, Collins model, liquid–gas phase diagram, binary system
PACC: 6470F, 8310D, 1240E

1. Introduction

In 1959, Bernal[1−3] presented a monatomic liquid geometrical theory. In this theory, the difference between the solid and the liquid lies in two points: the long-range order of a solid, and the short-range order and long-range disorder of a liquid. In 1964, according to the theory of Bernal,[4] Collins[5] presented a simplified Bernal model that is also called the Collins model. Based on the Collins model, Kawamura [6,7] and Do *et al*[8−11] have studied the properties of a two-dimensional (2D) system, and the whole phase diagram of the 2D system was obtained, which was quite similar to the 3D system. Also, Do *et al* generalized this model into a two-component system, and the solid-liquid phase diagrams obtained are quite analogous to the typical binary phase diagram for a real system. But they considered only the nearest neighbouring interaction, and regarded it as a constant potential. The liquid–gas coexistence is demonstrated by Abreham[18] and Mulero *et al*.[19] In this paper, we further introduced the Lennard-Jones (L-J) potential and the "molecular fraction" into the 2D alternative Collins binary system. The liquid–gas phase diagrams of the 2D alternative L-J binary system were obtained, and they are also quite analogous to the typical liquid–gas binary phase diagram in a real system.

2. Model

Collins model[1−6] is a close-packed system of equilateral triangles and squares in a plane. Using this model, the 2D monatomic L-J system has been studied in some papers.[12,16,17] Now suppose there are two components a and b, whose distribution on the lattice site is entirely disordered. In accordance with the packed form of the triangles and squares, there are four possibilities for the local configurations around a given atom, these are called the 4-atom, 5α-atom, 5β-atom and 6-atom configurations, as shown in Fig.1.

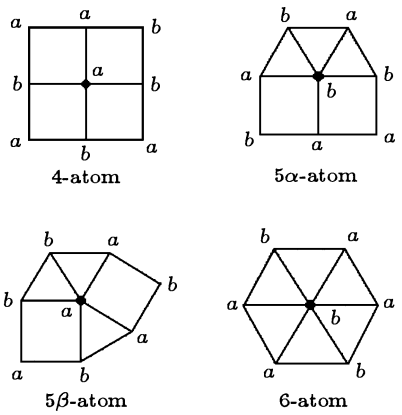


Fig.1. Four local atomic configurations.

Suppose N is the total number of atoms in a system, N_a and N_b are the numbers of the components a and b, respectively. N_{ar} and N_{br} are the numbers of r-atoms of components a and b, respectively (r=4,

5α, 5β and 6). We have

$$\begin{aligned} N =& N_a + N_b \\ =& N_{a4} + N_{a5\alpha} + N_{a5\beta} + N_{a6} \\ &+ N_{b4} + N_{b5\alpha} + N_{b5\beta} + N_{b6}. \end{aligned} \tag{1}$$

Writing $N_{ar}/N = n_{ar}$ and $N_{br}/N = n_{br}$, Eq.(1) becomes

$$n_{a4} + n_{a5\alpha} + n_{a5\beta} + n_{a6} + n_{b4} + n_{b5\alpha} + n_{b5\beta} + n_{b6} = 1. \tag{2}$$

We introduce the parameters x, y, m, z and Q, which satisfy the following relations

$$\begin{aligned} n_{5\alpha} + n_{5\beta} = x, \qquad & n_{5\alpha} = mx, \\ n_{5\beta} = (1-m)x, \qquad & n_4 = y, \\ n_6 = 1 - x - y, \qquad & n_a = z, \\ n_b = 1 - z, \qquad & Q = N/L, \end{aligned} \tag{3}$$

where L is the total number of lattice sites and Q is called the molecular fraction. Also we have $n_r = n_{ar} + n_{br}$ (r=4, 5α, 5β and 6).

3. Gibbs free energy

From thermodynamics, Gibbs free energy of a system can be written as

$$G = U - TS + PA, \tag{4}$$

where U and S represent the internal energy and the entropy of the system, respectively; T is the temperature; A is the area; and P is the pressure (having the dimension of force per unit length) of the 2D system.

Suppose the attractive interaction between the atom pairs is the L-J potential $\phi(r_j)$,[13]

$$\phi(r_j) = 4\varepsilon[(\sigma/r_j)^{12} - (\sigma/r_j)^6], \tag{5}$$

where σ is the hard-disc diameter of the close-packed system, r_j is the distance between atoms, and $-\varepsilon$ is the minimum of the potential, as shown in Fig.2.

Since the L-J interaction approaches zero as $1/r^6$ for atoms at large separations, we consider only seven kinds of distance between atoms,[12] which are smaller than $\sqrt{7}b$ (where b is the distance between the nearest neighbouring lattice sites). They are r_j (j=1, 2,3,4,5,6,7), i.e. $r_j = b$, $\sqrt{2}b$, $\sqrt{3}b$, $\sqrt{2+\sqrt{3}}b$, $2b$, $\sqrt{5}b$ and $\sqrt{4+\sqrt{3}}b$. If we considered the atom thermal vibration around the lattice point and the molecular fraction Q, then the internal energy U of the 2D system is given by

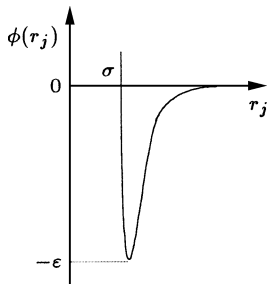


Fig.2. L-J interaction.

$$\begin{aligned} U/Nk_{\rm B}T =& \frac{1}{Nk_{\rm B}T}\sum_{j=1}^{7} N_j\{4\varepsilon_{aa}[(\sigma/r_j)^{12} - (\sigma/r_j)^6]z^2 \\ &+ 4\varepsilon_{ab}[(\sigma/r_j)^{12} - (\sigma/r_j)^6]2z(1-z) \\ &+ 4\varepsilon_{bb}[(\sigma/r_j)^{12} - (\sigma/r_j)^6](1-z)^2\}Q + 1 \\ =& (1/k_{\rm B}T)\{[k_{f1}(\sigma/b)^{12} - k_{f2}(\sigma/b)^6] \\ &\times [z\varepsilon_{aa} + (1-z)\varepsilon_{bb} - z(1-z)\varepsilon]\}Q + 1, \end{aligned} \tag{6}$$

where N_j is the number of atom pairs corresponding to the seven kinds of distance r_j (j=1,2,3,4,5,6,7); z^2, $(1-z)^2$ and $2z(1-z)$ are the possibilities of forming a-a, b-b and a-b (or b-a) atom pairs, respectively; k_{f1} and k_{f2} are written as

$$\begin{aligned} k_{f1} &= 12.0194 + 0.0014mx - 1.9484x - 3.8914y, \\ k_{f2} &= 12.6319 + 0.0144mx - 1.7926x - 3.3789y; \end{aligned} \tag{7}$$

$-\varepsilon_{aa}$, $-\varepsilon_{bb}$ and $-\varepsilon_{ab}$ are the minima of the potentials for the a-a, b-b and a-b (or b-a) atom pairs, respectively; $k_{\rm B}$ is Boltzmann constant; ε is the mixed energy, $\varepsilon = \varepsilon_{aa} + \varepsilon_{bb} - 2\varepsilon_{ab}$.

Considering the influence of thermal vibration and the existence of holes in the system, the entropy of the system S is obtained by using the same method employed in Refs.[8]–[12], [14] and [15], it is

$$\begin{aligned} S/Nk_{\rm B} =& (S_{\rm config} + S_{\rm heat} + S_{\rm hole})/Nk_{\rm B} \\ =& -f(m,x,y) - z\ln z - (1-z)\ln(1-z) \\ &+ z\ln(2\pi M_a k_{\rm B}T/h^2) \\ &+ (1-z)\ln(2\pi M_b k_{\rm B}T/h^2) \\ &+ \ln(2\sqrt{3}\alpha^2\sigma^2) - \ln Q - \frac{1-Q}{Q}\ln(1-Q). \end{aligned} \tag{8}$$

Then the Gibbs free energy G and the free energy F can be expressed as

$$\begin{aligned} &F/Nk_{\rm B}T \\ =&(1/k_{\rm B}T)[k_{f1}(\sigma/b)^{12}-k_{f2}(\sigma/b)^{6}] \\ &\times[z\varepsilon_{aa}+(1-z)\varepsilon_{bb}-z(1-z)\varepsilon]Q+f(m,x,y) \\ &+z\ln z+(1-z)\ln(1-z)-z\ln(2\pi M_a k_{\rm B}T/h^2) \\ &-(1-z)\ln(2\pi M_b k_{\rm B}T/h^2) \\ &-\ln(2\sqrt{3}\alpha^2\sigma^2)-\ln\{[1+C(x+2y)]Q\} \\ &+\ln Q+\frac{1-Q}{Q}\ln(1-Q), \end{aligned} \tag{9}$$

and

$$\begin{aligned} G/Nk_{\rm B}T =&F/Nk_{\rm B}T+(PA_0/Nk_{\rm B}T) \\ &\times[1+C(x+2y)](b/\sigma)^2/Q, \end{aligned} \tag{10}$$

where

$$\begin{aligned} f(m,x,y) =&y\ln y+mx\ln(mx) \\ &+(1-m)x\ln[(1-m)x] \\ &+[1-(x+y)]\ln[1-(x+y)] \\ &-\frac{1}{2}(4y+mx)\ln(y+mx) \\ &-(2-m)x\ln x-(x+2y)\ln(x+y) \\ &-\frac{1}{2}[6+(m-5)x-6y]\ln(1-y), \end{aligned} \tag{11}$$

and $\alpha=b/\sigma-1$, M_a is the mass of an a atom, M_b is the mass of a b atom, h is the Planck constant and $C=(2\sqrt{3}-3)/6$.

According to our model, when $x\neq 0$, the system corresponds to liquid phase or a gas phase,[9,10,17] and Eq.(10) represents the Gibbs free energy of the 2D binary system in a liquid phase or gas phase. Of course, it is determined by the molecular fraction Q, whether the system is a liquid phase or a gas phase. If we minimize the Gibbs free energy with respect to Q, then by using the relation $\dfrac{\partial}{\partial Q}\left(\dfrac{G}{Nk_{\rm B}T}\right)=0$ and Eqs.(9)–(11), we have

$$\begin{aligned} &(1/k_{\rm B}T)[k_{f1}(\sigma/b)^{12}-k_{f2}(\sigma/b)^{6}] \\ &\times[z\varepsilon_{aa}+(1-z)\varepsilon_{bb}-z(1-z)\varepsilon]+1/Q \\ &-(1/Q^2)\ln(1-Q)-(PA_0/Nk_{\rm B}T) \\ &\times[1+C(x+2y)](b/\sigma)^2/Q^2=0. \end{aligned} \tag{12}$$

We now consider the region at low temperatures and low pressures. The required conditions for T and P are

$$\begin{aligned} &\exp\{(1/k_{\rm B}T)[k_{f1}(\sigma/b)^{12}-k_{f2}(\sigma/b)^{6}] \\ &\times[z\varepsilon_{aa}+(1-z)\varepsilon_{bb}-z(1-z)\varepsilon]+1\}\ll 1, \end{aligned}$$

and

$$(PA_0/2Nk_{\rm B}T)[1+C(x+2y)](b/\sigma)^2\ll 1. \tag{13}$$

Using these conditions, the Eq.(12) has two solutions. One is $Q\approx 0$, corresponding to the gas phase, and the other is $Q\approx 1$, corresponding to the liquid phase. These equations can be written as

$$\begin{aligned} Q\approx&1-\exp\{(1/k_{\rm B}T)[k_{f1}(\sigma/b)^{12}-k_{f2}(\sigma/b)^{6}] \\ &\times[z\varepsilon_{aa}+(1-z)\varepsilon_{bb}-z(1-z)\varepsilon]+1\}, \end{aligned} \tag{14}$$

and

$$Q\approx(PA_0/2Nk_{\rm B}T)[1+C(x+2y)](b/\sigma)^2. \tag{15}$$

Suppose t$=k_{\rm B}T/\varepsilon^{\rm l}$ and $p=PA_0/N\varepsilon^{\rm l}$ (where $\varepsilon^{\rm l}$ is the mixed energy of the liquid phase), i.e. the normalized temperature and the normalized pressure, respectively. Substituting Eqs.(14) and (15) into Eqs.(9) and (10), respectively, the first-order approximate expressions of the normalized free energy f and the normalized Gibbs free energy g can be obtained for the liquid and gas phases, respectively. These equations are

$$\begin{aligned} f^{\rm l}\approx&(1/t)[k_{f1}(\sigma/b^{\rm l})^{12}-k_{f2}(\sigma/b^{\rm l})^{6}] \\ &\times[z^{\rm l}\varepsilon^{\rm l}_{aa}/\varepsilon^{\rm l}+(1-z^{\rm l})\varepsilon^{\rm l}_{bb}/\varepsilon^{\rm l}-z^{\rm l}(1-z^{\rm l})] \\ &+f(m,x,y)+z^{\rm l}\ln z^{\rm l}+(1-z^{\rm l})\ln(1-z^{\rm l}) \\ &-z^{\rm l}\ln(2\pi M_a k_{\rm B}T/h^2) \\ &-(1-z^{\rm l})\ln(2\pi M_b k_{\rm B}T/h^2)-\ln(2\sqrt{3}\sigma^2) \\ &-\ln[1+C(x+2y)]-2\ln(b^{\rm l}/\sigma-1) \\ &-\exp\{(1/t)[k_{f1}(\sigma/b^{\rm l})^{12}-k_{f2}(\sigma/b^{\rm l})^{6}] \\ &\times[z^{\rm l}\varepsilon^{\rm l}_{aa}+(1-z^{\rm l})\varepsilon^{\rm l}_{bb}-z^{\rm l}(1-z^{\rm l})]+1\}, \end{aligned} \tag{16}$$

$$g^{\rm l}\approx f^{\rm l}+(p/t)(b^{\rm l}/\sigma)^2[1+C(x+2y)], \tag{17}$$

$$\begin{aligned} f^{\rm g}\approx&(p/2t^2)[k_{f1}(\sigma/b^{\rm g})^{12}-k_{f2}(\sigma/b^{\rm g})^{6}] \\ &\times[z^{\rm g}\varepsilon^{\rm g}_{aa}/\varepsilon^{\rm l}+(1-z^{\rm g})\varepsilon^{\rm g}_{bb}/\varepsilon^{\rm l} \\ &-z^{\rm g}(1-z^{\rm g})\varepsilon^{\rm g}/\varepsilon^{\rm l}](b^{\rm g}/\sigma)^2[1+C(x+2y)] \\ &+f(m,x,y)+z^{\rm g}\ln z^{\rm g}+(1-z^{\rm g})\ln(1-z^{\rm g}) \\ &-z^{\rm g}\ln(2\pi M_a k_{\rm B}T/h^2) \\ &-(1-z^{\rm g})\ln(2\pi M_b k_{\rm B}T/h^2) \\ &-2\ln(b^{\rm g}/\sigma-1)-\ln(2\sqrt{3}\sigma^2) \\ &+\ln[1+C(x+2y)]+2\ln[(p/2t)(b^{\rm g}/\sigma)^2] \\ &+(p/2t)[1+C(x+2y)](b^{\rm g}/\sigma)^2-1, \end{aligned} \tag{18}$$

$$g^{\rm g}\approx f^{\rm g}+2, \tag{19}$$

where the superscripts l and g denote the liquid and gas phases, respectively.

4. Liquid-gas phase diagram

According to the thermodynamic conditions for describing the coexistence of two phases in a binary system, we have

$$f^{\mathrm{l}} - z\frac{\partial f^{\mathrm{l}}}{\partial z^{\mathrm{l}}} = f^{\mathrm{g}} - z^{\mathrm{g}}\frac{\partial f^{\mathrm{g}}}{\partial z^{\mathrm{g}}},$$

$$f^{\mathrm{l}} - (1-z^{\mathrm{l}})\frac{\partial f^{\mathrm{l}}}{\partial (1-z^{\mathrm{l}})} = f^{\mathrm{g}} - (1-z^{\mathrm{g}})\frac{\partial f^{\mathrm{g}}}{\partial (1-z^{\mathrm{g}})}. \quad (20)$$

The Gibbs free energy should also satisfy the stability conditions of phase equilibrium, they are

$$\frac{\partial g^i}{\partial(\sigma/b^i)} = 0, \quad \frac{\partial^2 g^i}{\partial(\sigma/b^i)^2} > 0 \quad (i = \mathrm{l}, \mathrm{g}); \quad (21)$$

$$\frac{\partial g^j}{\partial j} = 0, \quad \frac{\partial^2 g^j}{\partial j^2} > 0 \quad (j = n, x, y). \quad (22)$$

If we substitute the Eqs.(16)–(19) to Eqs.(20)–(22), we can gain a group of the seven equations. We choose two different groups of values of attractive interactions $\varepsilon^{\mathrm{l}}_{aa}/\varepsilon^{\mathrm{l}}$, $\varepsilon^{\mathrm{l}}_{bb}/\varepsilon^{\mathrm{l}}$, $\varepsilon^{\mathrm{g}}_{aa}/\varepsilon^{\mathrm{l}}$, $\varepsilon^{\mathrm{g}}_{bb}/\varepsilon^{\mathrm{l}}$ and $\varepsilon^{\mathrm{g}}/\varepsilon^{\mathrm{l}}$, and the normalized pressures are both fixed at p=0.08. The cigar-type liquid–gas phase diagram and the liquid–gas phase diagram with a congruent maximum point can be obtained, as shown in Figs.3 and 4, respectively.

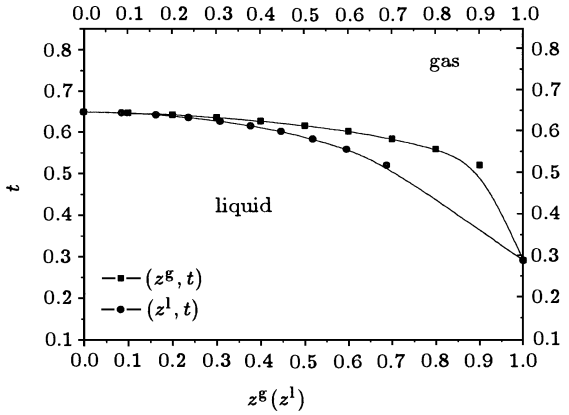


Fig.3. The cigar-type liquid–gas phase diagram. The values taken for the normalized pressure and the attractive interactions were: p=0.08, $\varepsilon^{\mathrm{l}}_{aa}/\varepsilon^{\mathrm{l}}$=–0.005, $\varepsilon^{\mathrm{l}}_{bb}/\varepsilon^{\mathrm{l}}$=–1.05, $\varepsilon^{\mathrm{g}}_{aa}/\varepsilon^{\mathrm{l}}$=–0.004, $\varepsilon^{\mathrm{g}}_{bb}/\varepsilon^{\mathrm{l}}$=–1.0 and $\varepsilon^{\mathrm{g}}/\varepsilon^{\mathrm{l}}$=0.0005.

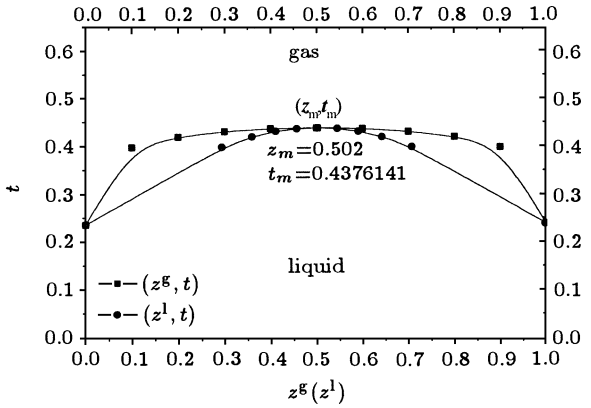


Fig.4. The liquid–gas phase diagram with a congruent maximum point. The values taken for the normalized pressure and the attractive interactions were: p=0.08, $\varepsilon^{\mathrm{l}}_{aa}/\varepsilon^{\mathrm{l}}$=–0.005, $\varepsilon^{\mathrm{l}}_{bb}/\varepsilon^{\mathrm{l}}$=–0.0015, $\varepsilon^{\mathrm{g}}_{aa}/\varepsilon^{\mathrm{l}}$=–0.001, $\varepsilon^{\mathrm{g}}_{bb}/\varepsilon^{\mathrm{l}}$=–0.004 and $\varepsilon^{\mathrm{g}}/\varepsilon^{\mathrm{l}}$=0.005.

5. Discussions

Kawamura[6,7] and Do *et al*[8,9] have studied the 2D Collins model in a monatomic system and also in a binary system. But they considered only the nearest neighbouring interaction, and regarded it as a constant potential. Their results could be considered to be rough and unreasonable, and they cannot be compared with the real system. Yi and others[12,16] introduced the L-J potential into the 2D Collins model system, however, they studied only the monatomic system and the solid-liquid phase transition. We have introduced the L-J potential and the molecular fraction into a 2D binary system. This is an improvement on the basis of their study. Using the L-J potential and the molecular fraction, we have studied the monatomic system,[17] and in this paper we have further investigated the binary system and the liquid–gas transition. We find that the phase diagrams obtained, as shown in Figs.3 and 4, are quite analogous to the liquid–gas phase diagram in a real binary system.[20] The theoretical results show that this improvement should be considered to be more reliable and reasonable. We can see that, if the attractive interactions are chosen properly, the more complicated binary phase diagrams can be obtained too. In particular, we must emphasize that our study is based on an ideal theoretical model. Here we have discussed only two simple types of phase diagrams. How to choose the attractive interactions reasonably will be discussed in a future paper.

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