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2001 J. Phys.: Condens. Matter 13 6075

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The two-dimensional monatomic Leonard-Jones system: triple point and critical point

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Received 29 January 2001, in final form 21 March 2001

Published 22 June 2001

Online at stacks.iop.org/JPhysCM/13/6075

Abstract

We introduce a Leonard-Jones (L-J) interaction into the two-dimensional (2D) Collins model, and consider the existence of the holes that are called the molecular fraction. The Gibbs free energy of solid, liquid and gas has been derived. From the Gibbs function we have obtained the whole diagram of the 2D monatomic L-J system, which includes the melting line, vaporization line, sublimation line and the triple point. Also, we have discussed a few properties of the critical point.

1. Introduction

In 1964, Collins [1] presented a simplified Bernal model [2], this (Collins) model not only stresses features of the solid (long-range order), but also features of the liquid (short-range order and long-range disorder). The advantage of this model is that the complicated thermal properties can be expressed by means of a simplified physics model. On the basis of this model, Kawamura [3, 4] and Do Yi-Jing *et al* [5, 6] studied the properties of a two-dimensional (2D) system, which was quite similar to the 3D system [10]. However, their studies are all limited to the nearest-neighbour interaction, which is a constant, so the results of their study have only qualitative meaning, and cannot be compared with real systems. In 1982 the melting phase transition of Ar, Kr, Xe submonolayers were first determined uniformly by synchrotron x-ray diffraction, and a set of reliable triple point temperatures was obtained [7]. Then You-min Yi *et al* [11] introduced the L-J potential into the Collins model, considering the next-nearest and next-neighbours interaction, and gave the melting line. The results are close to experimental results. Rui-lun Zheng *et al* also introduced the L-J potential into the Collins model and studied the Boyle curve of a 2D fluid system and the solubility curve of a binary system [17, 18], but they did not give the whole diagram of the 2D monatomic L-J system.

On the basis of introducing the L-J potential into a 2D monatomic system, we consider the existence of holes and give further studies on the phase transitions between liquid–gas and solid–gas. Then the triple point is obtained. Also, we have discussed a few properties

of the critical point. The results of our work are quite analogous to a Monte Carlo computer simulation diagram and close to the experiment results of an inert gas.

2. Model

The Collins model is a close-packed system of equilateral triangles and squares in one plane. In accordance with the packed form of triangles and squares, we can divide the atoms of the system into four local structures, which are called 4-atom, 6-atom, 5α -atom and 5β -atom and are shown in figure 1.

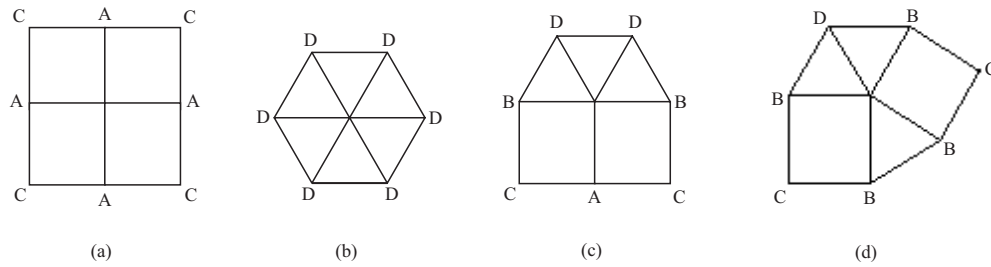


Figure 1. The four local atomic structures: (a) 4-atom, (b) 6-atom, (c) 5α -atom and (d) 5β -atom.

Suppose N is the total number of atoms in the system, N_r is the number of r -atoms ($r = 4, 5\alpha, 5\beta$ and 6), then

$$N_4 + N_{5\alpha} + N_{5\beta} + N_6 = N. \quad (1)$$

Writing $N_r/N = n_r$, we have

$$n_4 + n_{5\alpha} + n_{5\beta} + n_6 = 1. \quad (2)$$

For convenience, we introduce parameters x , y and m , which satisfy the following relations:

$$n_4 = y \quad n_{5\alpha} = mx \quad n_{5\beta} = (1 - m)x \quad n_6 = 1 - (x + y). \quad (3)$$

If α_r represents the area of one r -atom Wigner–Seitz cell, the total area of the system A can be written as

$$A = N_4 a_4 + n_{5\alpha} a_{5\alpha} + N_{5\beta} a_{5\beta} + N_6 a_6 \quad (4)$$

where $a_4 = b^2$, $a_{5\alpha} = a_{5\beta} = ((2 + \sqrt{3})/4)b^2$, $a_6 = (\sqrt{3}/2)b^2$, and b is the distance between the nearest-neighbour lattice sites. From equations (3) and (4) we get

$$A = [(2 - \sqrt{3})(x + 2y)/4 + \sqrt{3}/2]b^2 N. \quad (5)$$

3. Gibbs free energy

From thermodynamics, the Gibbs free energy of the 2D system can be written as

$$G = U - TS + PA \quad (6)$$

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

Suppose the attraction interaction between the atom pairs is the L-J potential $\Phi(r_j)$, r_j is the distance between the atoms and the potential energy E is given by

$$E = \sum_j N_j \Phi(r_j) \quad (7)$$

where

$$\Phi(r_j) = 4\varepsilon \left[\left(\frac{\sigma}{r_j} \right)^{12} - \left(\frac{\sigma}{r_j} \right)^6 \right] \quad (8)$$

N_j is the number of atom pairs whose distance is r_j , σ is the hard-disc diameter of the close-packed system and $-\varepsilon$ is the minimum of the potential (see figure 2).

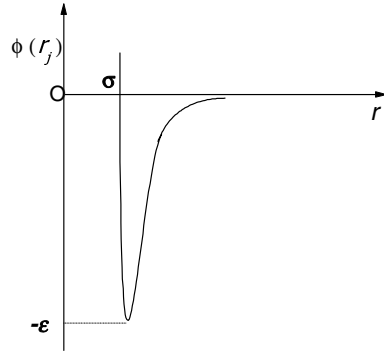


Figure 2. L-J interaction.

Table 1. The seven kinds of distance of the atom pairs r_j and the corresponding number of atom pairs N_j .

j	r_j	N_j
1	b	$(5N_{5\alpha} + 5N_{5\beta} + 4N_4 + 6N_6)/2$
2	$\sqrt{2}b$	$(2N_{5\alpha} + 2N_{5\beta} + 4N_4)/2$
3	$\sqrt{3}b$	$(2N_{5\alpha} + N_{5\beta} + 6N_6)/2$
4	$\sqrt{2 + \sqrt{3}}b$	$(4N_{5\alpha} + 8N_{5\beta})/2$
5	$2b$	$(2N_{5\alpha} + 4N_4 + 6N_6)/2$
6	$\sqrt{5}b$	$(2N_{5\alpha} + 8N_4)/2$
7	$\sqrt{4 + \sqrt{3}}b$	$(4N_{5\alpha} + 4N_{5\beta})/2$

As the L-J interaction approaches zero as $1/r^6$ at large distances the contribution of those atom pairs with large distances to the total potential can be neglected. From [11], in order to calculate accurately enough the potential energy E , we only consider seven kinds of distance of the atom pairs which are smaller than $\sqrt{7}b$. They are $r_j = b, \sqrt{2}b, \sqrt{3}b, \sqrt{2 + \sqrt{3}}b, 2b, \sqrt{5}b$ and $\sqrt{4 + \sqrt{3}}b$. The seven kinds of distance r_j ($j = 1, 2, \dots, 7$) and the corresponding number of atom pairs N_j ($j = 1, 2, \dots, 7$) are included in table 1.

Further considering the atom thermal vibration around the lattice point, using table 1 and equations (3), (7) and (8), the total internal energy of the system U can be written as

$$\frac{U}{NK_B T} = \frac{E}{NK_B T} + 1 = \frac{\varepsilon}{K_B T} \sum_{j=1}^7 4 \frac{N_j}{N} \left[\left(\frac{\sigma}{r_j} \right)^{12} - \left(\frac{\sigma}{r_j} \right)^6 \right] + 1$$

$$= \frac{\varepsilon}{K_B T} \left[k_{f1} \left(\frac{\sigma}{b} \right)^{12} - k_{f2} \left(\frac{\sigma}{b} \right)^6 \right] + 1 \quad (9)$$

where K_B is the Boltzmann constant and k_{f1} and k_{f2} are

$$\begin{aligned} k_{f1} &= 12.0194 + 0.0014mx - 1.9484x - 3.8914y \\ k_{f2} &= 12.6319 + 0.0144mx - 1.7926x - 3.2789y. \end{aligned} \quad (10)$$

The entropy of the system S derived from two parts: one, which is denoted S_{config} , is the contribution from the disorder associated with the arrangement of the triangles and the squares; the other, which is denoted S_{heat} , is the contribution of the thermal vibration of atoms around the lattice point to the entropy. We write the entropy, S , as

$$S = S_{config} + S_{heat} \quad (11)$$

where the configuration entropy S_{config} is

$$S_{config} = K_B \ln W_1 \quad (12)$$

where W_1 is the number of ways to arrange the four local structures of atoms in a plane. From statistical theory, W_1 can be represented as [5]

$$\begin{aligned} W_1 &= \frac{N!}{N_4! N_{5\alpha}! N_{5\beta}! N_6!} (n_4 + n_{5\alpha})^{(4N_4 + N_{5\alpha})/2} (n_{5\alpha} + n_{5\beta})^{(2N_{5\alpha} + 4N_{5\beta})/2} \\ &\quad \times (n_4 + n_{5\alpha} + n_{5\beta})^{(2N_{5\alpha} + 2N_{5\beta} + 4N_4)/2} (n_{5\alpha} + n_{5\beta} + n_6)^{(6N_6 + 2N_{5\alpha} + N_{5\beta})/2} \end{aligned} \quad (13)$$

where $N!/N_4!N_{5\alpha}!N_{5\beta}!N_6!$ is the number of ways of arranging the four kinds of atoms quite at random, and the remaining factor is a correction due to the geometrical constraints in the neighbouring sites. We can divide the lattices into four groups, as shown in figure 1. The lattice point A can only be formed in a 4-atom or 5 α -atom. The lattice point B can only be formed in a 5 α -atom or 5 β -atom. The lattice point C can only be formed in a 4-atom or 5 α -atom or 5 β -atom. The lattice point D can only be formed in a 5 α -atom, 5 β -atom or a 6-atom. So we must multiply the possibility that correct configurations appear in the neighbours. The last four factors of equation (13) are the corrections due to these constraints. Using equations (3), (12), (13) and the Stirling formula, we get

$$\begin{aligned} \frac{S_{config}}{N K_B} &= -y \ln y - mx \ln(mx) - (1-m)x \ln[(1-m)x] \\ &\quad - [1 - (x+y)] \ln[1 - (x+y)] + \frac{1}{2} (4y + mx) \ln(y + mx) \\ &\quad + (2-m)x \ln x + (x+2y) \ln(x+y) + \frac{1}{2} [6 + (m-5)x - 6y] \ln(1-y). \end{aligned} \quad (14)$$

On the other hand, S_{heat} is due to thermal vibrations, and is related to the free area of the atom vibration. Using the free volume theory [13–15], and supposing

$$a = \frac{b}{\sigma} - 1 \quad (15)$$

we obtain the mean free area of the atom \bar{a}_f , which is [5]

$$\bar{a}_f = 2\sqrt{3}\alpha^2\sigma^2[1 + C(x+y)] \quad (16)$$

where

$$C = (2\sqrt{3} - 3)/6.$$

Then we have

$$\frac{S_{heat}}{NK_B} = \ln[(2\pi MK_B T/h^2)\bar{a}_f] + 1 = \ln(2\pi MK_B T/h^2) + \ln(2\sqrt{3}\alpha^2\sigma^2) + \ln[1 + C(x + 2y)] + 1 \quad (17)$$

where M is the mass of an atom and h is the Planck constant.

Suppose the total area of the system at the close-packing A_0 is denoted by $A_0 = (\sqrt{3}/2)\sigma^2 N$. Then, using equations (5) and (15), we have the total area A as

$$A/A_0 = [1 + C(x + 2y)](1 + \alpha)^2 \quad (18)$$

so the PA term in equation (6) is given by

$$\frac{PA}{NK_B T} = \frac{PA_0}{NK_B T} [1 + C(x + 2y)](1 + \alpha)^2. \quad (19)$$

If we let $t = K_B T/\varepsilon$, $p = PA_0/N\varepsilon$, which represent the normalized temperature and the normalized pressure respectively, and using equations (6), (9), (11), (14), (17) and (19) the Gibbs free energy of the system can be written as

$$\begin{aligned} \frac{G}{N\varepsilon t} &= \frac{U}{NK_B T} - \frac{T(S_{config} + S_{heat})}{NK_B T} + \frac{PA}{NK_B T} \\ &= f(m, x, y) + \frac{1}{t} \left[k_{f1} \left(\frac{\sigma}{b} \right)^{12} - k_{f2} \left(\frac{\sigma}{b} \right)^6 \right] - \ln[1 + C(x + 2y)] \\ &\quad - 2 \ln \left(\frac{b}{\sigma} - 1 \right) + \frac{p}{t} [1 + C(x + 2y)] \left(\frac{b}{\sigma} \right)^2 + D(t) \end{aligned} \quad (20)$$

where

$$\begin{aligned} f(m, x, y) &= y \ln y + mx \ln(mx) + (1 - m)x \ln[(1 - m)x] + [1 - (x + y)] \ln[1 - (x + y)] \\ &\quad - \frac{1}{2}(4y + mx) \ln(y + mx) - (2 - m)x \ln x - (x + 2y) \ln(x + y) \\ &\quad - \frac{1}{2}[6 + (m - 5)x - 6y] \ln(1 - y) \end{aligned} \quad (21)$$

and

$$D(t) = \ln(2\pi M\varepsilon t/h^2) + \ln(2\sqrt{3}\sigma^2). \quad (22)$$

If the hard-disc diameter of the system σ is a constant, when t is fixed $D(t)$ is obviously a constant too.

Now, let us study the position of the phase transition point between solid and liquid. According to the Collins model, when $x \neq 0$, because of the existence of the 5-atom structure, the system shows short-range order, corresponding to the liquid; when $x = 0$, the system corresponds to a solid. Using equation (20) we get the Gibbs free energy of liquid and solid respectively:

$$\begin{aligned} \frac{G^f}{N\varepsilon t} &= f(m, x, y) + \frac{1}{t} \left[k_{f1} \left(\frac{\sigma}{b_f} \right)^{12} - k_{f2} \left(\frac{\sigma}{b_f} \right)^6 \right] - \ln[1 + C(x + 2y)] \\ &\quad - 2 \ln \left(\frac{b_f}{\sigma} - 1 \right) + \frac{p}{t} [1 + C(x + 2y)] \left(\frac{b_f}{\sigma} \right)^2 + D(t) \end{aligned} \quad (23)$$

$$\begin{aligned} \frac{G^s}{N\varepsilon t} &= f(y) + \frac{1}{t} \left[k_{s1} \left(\frac{\sigma}{b_s} \right)^{12} - k_{s2} \left(\frac{\sigma}{b_s} \right)^6 \right] - \ln(1 + 2Cy) \\ &\quad - 2 \ln \left(\frac{b_s}{\sigma} - 1 \right) + \frac{p}{t} (1 + 2Cy) \left(\frac{b_s}{\sigma} \right)^2 + D(t) \end{aligned} \quad (24)$$

where b_f and b_s are the distance between the nearest-neighbour lattice sites corresponding to the liquid and solid, respectively. From equations (10) and (21), $f(y)$, k_{S_1} and k_{S_2} are

$$\begin{aligned} f(y) &= -3y \ln y - 2(1-y) \ln(1-y) \\ k_{S_1} &= 12.0194 - 3.8914y \quad k_{S_2} = 12.6319 - 3.3789y. \end{aligned} \quad (21a)$$

At the position of the phase transition point, the Gibbs function must satisfy stability conditions and the phase transition equation, which are

$$\frac{G^f}{N\epsilon t} = \frac{G^s}{N\epsilon t} \quad (25)$$

$$\frac{\partial}{\partial x} \left(\frac{G^f}{N\epsilon t} \right) = 0 \quad \frac{\partial^2}{\partial x^2} \left(\frac{G^f}{N\epsilon t} \right) > 0 \quad (26)$$

$$\frac{\partial}{\partial m} \left(\frac{G^f}{N\epsilon t} \right) = 0 \quad \frac{\partial^2}{\partial m^2} \left(\frac{G^f}{N\epsilon t} \right) > 0 \quad (27)$$

$$\frac{\partial}{\partial y} \left(\frac{G^f}{N\epsilon t} \right) = 0 \quad \frac{\partial^2}{\partial y^2} \left(\frac{G^f}{N\epsilon t} \right) > 0 \quad (28)$$

$$\frac{\partial}{\partial(\sigma/b_f)} \left(\frac{G^f}{N\epsilon t} \right) = 0 \quad \frac{\partial^2}{\partial(\sigma/b_f)^2} \left(\frac{G^f}{N\epsilon t} \right) > 0 \quad (29)$$

$$\frac{\partial}{\partial(\sigma/b_s)} \left(\frac{G^s}{N\epsilon t} \right) = 0 \quad \frac{\partial^2}{\partial(\sigma/b_s)^2} \left(\frac{G^s}{N\epsilon t} \right) > 0. \quad (30)$$

Using equations (25)–(30), if we fix the normalized temperature t , the values of the parameters m^* , x^* , y^* , $(b_f/\sigma)^*$, $(b_s/\sigma)^*$ and p^* at the transition point can be calculated, as shown in table 2 (the superscript * means the transition point).

Table 2. Values of the parameters at the transition point.

t	m^*	x^*	y^*	$(b_f/\sigma)^*$	$(b_s/\sigma)^*$	p^*
0.99	0.5777	0.8926	0.0077	1.139 852	1.142 763	4.163 794
0.9	0.5776	0.8932	0.0078	1.143 072	1.145 372	3.386 817
0.8	0.5805	0.8923	0.0079	1.146 593	1.148 062	2.580 564
0.7	0.5808	0.8937	0.0080	1.151 783	1.152 066	1.719 278
0.6	0.5832	0.8921	0.0081	1.155 550	1.154 577	1.000 144
0.55	0.5827	0.8936	0.0083	1.159 619	1.157 510	0.560 79
0.5	0.5821	0.8925	0.0082	1.161 582	1.158 625	0.231 25

4. Triple point and critical point

To continue further study of the transition between solid, liquid and gas, we suppose there are holes in the system and define the molecular fraction Q :

$$Q = N/L \quad (31)$$

where L is the total number of lattice point and N is the total number of atoms of the system. The disordered distribution of the holes contributes to the entropy of the system, that is

$$S_{hole} = K_B \ln W_2$$

where

$$W_2 = L!/N!(L-N)!$$

Also using the Stirling formula, we get

$$\frac{S_{hole}}{NK_B} = -\ln Q - \frac{1-Q}{Q} \ln(1-Q). \quad (32)$$

So the total entropy is $S = S_{config} + S_{heat} + S_{hole}$. Therefore, when the influence of the holes for the Gibbs free energy G is considered, equation (20) can be written anew as

$$\begin{aligned} \frac{G}{N\epsilon t} &= \frac{U}{NK_B T} Q - \frac{T(S_{config} + S_{heat} + S_{hole})}{NK_B T} + \frac{PA}{NK_B T} \frac{1}{Q} \\ &= f(m, x, y) + \ln Q + \frac{1-Q}{Q} \ln(1-Q) \\ &\quad + \frac{1}{t} \left[k_1 \left(\frac{\sigma}{b} \right)^{12} - k_2 \left(\frac{\sigma}{b} \right)^6 \right] Q - \ln\{[1 + C(x + 2y)]/Q\} \\ &\quad - 2 \ln \left(\frac{b}{\sigma} - 1 \right) + \frac{p}{t} [1 + C(x + 2y)] \left(\frac{b}{\sigma} \right)^2 / Q + D(t). \end{aligned} \quad (33)$$

Therefore, when $x = 0$ the Gibbs free energy at the transition point $G^0/N\epsilon t$ is

$$\begin{aligned} \frac{G^0}{N\epsilon t} &= f(y^*) + 2 \ln Q + \frac{1-Q}{Q} \ln(1-Q) + \frac{1}{t} \left[k_{s1} \left(\frac{\sigma}{b_s} \right)^{12} - k_{s2} \left(\frac{\sigma}{b_s} \right)^6 \right] Q \\ &\quad - \ln(1 + 2Cy^*) - 2 \ln \left[\left(\frac{b_s}{\sigma} \right)^* - 1 \right] + \frac{p}{t} (1 + 2Cy^*) \left(\frac{b_s}{\sigma} \right)^2 / Q + D(t). \end{aligned} \quad (34)$$

When $x = x^*$ the Gibbs free energy at the transition point $G^*/N\epsilon t$ is

$$\begin{aligned} \frac{G^*}{N\epsilon t} &= f(m^* x^* y^*) + 2 \ln Q + \frac{1-Q}{Q} \ln(1-Q) + \frac{1}{t} \left[k_{f1} \left(\frac{\sigma}{b_f} \right)^{12} - k_{f2} \left(\frac{\sigma}{b_f} \right)^6 \right] Q \\ &\quad - \ln[1 + c(x^* + 2y^*)] - 2 \ln \left[\left(\frac{b_f}{\sigma} \right)^* - 1 \right] \\ &\quad + \frac{p}{t} [1 + C(x^* + 2y^*)] \left(\frac{b_f}{\sigma} \right)^2 / Q + D(t). \end{aligned} \quad (35)$$

Equations (34) and (35) are both functions of Q . If we minimize the Gibbs free energy with respect to Q , using relations

$$\frac{\partial}{\partial Q} \left(\frac{G^0}{N\epsilon t} \right) = 0 \quad \text{and} \quad \frac{\partial}{\partial Q} \left(\frac{G^*}{N\epsilon t} \right) = 0$$

we get

$$\frac{1}{Q} - \frac{1}{Q^2} \ln(1-Q) + \frac{1}{t} \left[k_{s1} \left(\frac{\sigma}{b_s} \right)^{12} - k_{s2} \left(\frac{\sigma}{b_s} \right)^6 \right] - \frac{p}{t} (1 + 2Cy^*) \left(\frac{b_s}{\sigma} \right)^2 / Q^2 = 0 \quad (36)$$

$$\begin{aligned} \frac{1}{Q} - \frac{1}{Q^2} \ln(1-Q) + \frac{1}{t} \left[k_{f1} \left(\frac{\sigma}{b_f} \right)^{12} - k_{f2} \left(\frac{\sigma}{b_f} \right)^6 \right] \\ - \frac{p}{t} [1 + C(x^* + 2y^*)] \left(\frac{b_f}{\sigma} \right)^2 / Q^2 = 0. \end{aligned} \quad (37)$$

Let us consider the region at low temperature and low pressure including the triple point. The required conditions for t and p are

$$\frac{p}{2t} (1 + 2Cy) \left(\frac{b_i}{\sigma} \right)^2 \ll 1 \quad (i = f, s)$$

$$\exp \left\{ \frac{1}{t} \left[k_1 \left(\frac{\sigma}{b_i} \right)^{12} - k_2 \left(\frac{\sigma}{b_i} \right)^6 \right] + 1 \right\} \ll 1 \quad (i = f, s). \quad (38)$$

Under these conditions, equations (36) and (37) both have two solutions. One is Q close to zero and the other is Q close to unity. So there are four groups of results, which are

$$Q \approx \frac{p}{2t} (1 + 2Cy^*) \left(\frac{b_s}{\sigma} \right)^{*2} \quad x = 0 \quad (39)$$

$$Q \approx 1 - \exp \left\{ \frac{1}{t} \left[k_{s1} \left(\frac{\sigma}{b_s} \right)^{*12} - k_{s2} \left(\frac{\sigma}{b_s} \right)^{*6} \right] + 1 \right\} \quad x = 0 \quad (40)$$

$$Q \approx \frac{p}{2t} [1 + C(x^* + 2y^*)] \left(\frac{b_f}{\sigma} \right)^{*2} \quad x = x^* \quad (41)$$

$$Q \approx 1 - \exp \left\{ \frac{1}{t} \left[k_{f1} \left(\frac{\sigma}{b_f} \right)^{*12} - k_{f2} \left(\frac{\sigma}{b_f} \right)^{*6} \right] + 1 \right\} \quad x = x^*. \quad (42)$$

These results can all minimize the Gibbs free energy of the system. According to our model, when $x = 0$ and $Q \rightarrow 1$ the system corresponds to a solid, when $x = x^* \neq 0$ and $Q \rightarrow 1$ the system corresponds to a liquid and when $x = x^* \neq 0$ and $Q \rightarrow 0$ the system corresponds to a gas. So equation (39) corresponds to the 'unphysical' state (which we do not consider here), equation (40) corresponds to the solid state, equation (41) corresponds to the gas state and equation (42) corresponds to the liquid state. Substitution of (40) into (34) and of (41) and (42) into (35) gives the Gibbs free energy of a solid, gas and liquid, respectively. Under the low temperature and low pressure that satisfy condition (38), for simplicity we just give the approximate first-order expressions of the free energy of a solid, liquid and gas, respectively. These are

$$\begin{aligned} \frac{G^s}{N\epsilon t} &\cong \frac{1}{t} \left[k_{s1} \left(\frac{\sigma}{b_s} \right)^{*12} - k_{s2} \left(\frac{\sigma}{b_s} \right)^{*6} \right] + f(y^*) - 2 \exp \left\{ \frac{1}{t} \left[k_{s1} \left(\frac{\sigma}{b_s} \right)^{*12} - k_{s2} \left(\frac{\sigma}{b_s} \right)^{*6} \right] + 1 \right\} \\ &\quad - \ln(1 + 2Cy^*) - 2 \ln \left[\left(\frac{b_s}{\sigma} \right)^* - 1 \right] + \frac{p}{t} (1 + 2Cy^*) \left(\frac{b_s}{\sigma} \right)^{*2} + D(t) \end{aligned} \quad (43)$$

$$\begin{aligned} \frac{G^l}{N\epsilon t} &\cong \frac{1}{t} \left[k_{f1} \left(\frac{\sigma}{b_f} \right)^{*12} - k_{f2} \left(\frac{\sigma}{b_f} \right)^{*6} \right] + f(m^* x^* y^*) \\ &\quad - 2 \exp \left\{ \frac{1}{t} \left[k_{f1} \left(\frac{\sigma}{b_f} \right)^{*12} - k_{f2} \left(\frac{\sigma}{b_f} \right)^{*6} \right] + 1 \right\} \\ &\quad - \ln[1 + C(x^* + 2y^*)] - 2 \ln \left[\left(\frac{b_f}{\sigma} \right)^* - 1 \right] \\ &\quad + \frac{p}{t} [1 + C(x^* + 2y^*)] \left(\frac{b_f}{\sigma} \right)^{*2} + D(t) \end{aligned} \quad (44)$$

$$\begin{aligned} \frac{G^g}{N\epsilon t} &\cong \frac{1}{t} \left[k_{f1} \left(\frac{\sigma}{b_f} \right)^{*12} - k_{f2} \left(\frac{\sigma}{b_f} \right)^{*6} \right] \frac{p}{2t} [1 + C(x^* + 2y^*)] \left(\frac{b_f}{\sigma} \right)^{*2} + f(m^* x^* y^*) \\ &\quad + 2 \ln \left[\frac{p}{2t} \left(\frac{b_f}{\sigma} \right)^{*2} \right] + \ln[1 + C(x^* + 2y^*)] - 2 \ln \left[\left(\frac{b_f}{\sigma} \right)^* - 1 \right] \\ &\quad + \frac{p}{2t} [1 + C(x^* + 2y^*)] \left(\frac{b_f}{\sigma} \right)^{*2} + 1 + D(t) \end{aligned} \quad (45)$$

where the superscripts s , l and g represent the solid, liquid and gas states, respectively. Using the phase transition equation, the first-order approximation of the melting line, vaporization

line and sublimation line can be given immediately, and the first-order approximation of the triple point can also be deduced. The calculated results and the phase diagram are shown in figure 3. The position of the triple point is at about $t_t \approx 0.38$ and $p_t \approx 0.009$.

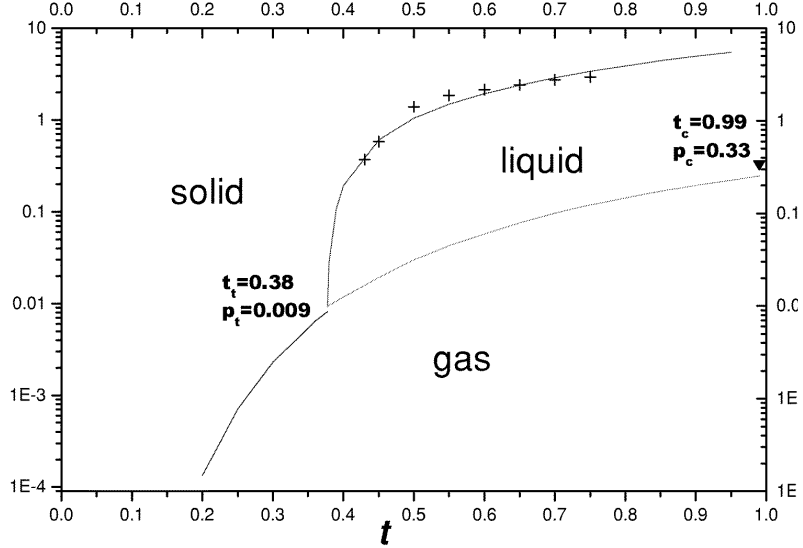


Figure 3. The phase diagram of a 2D monatomic L-J system, the full curve is the result of our present work, the crosses (+) are the Monte Carlo computer simulation results [9].

The critical point is the terminal point of the vaporization line. According to the Collins model, the gas and the liquid states both correspond to the Gibbs free energy when $x = x^*$. Using equation (37), we get

$$p = \left\{ \left[k_{f1} \left(\frac{\sigma}{b_f} \right)^{*12} - k_{f2} \left(\frac{\sigma}{b_f} \right)^{*6} \right] Q^2 - Qt \right. \\ \left. - t \ln(1 - Q) \right\} / \left\{ [1 + C(x^* + 2y^*)] \left(\frac{b_f}{\sigma} \right)^{*2} \right\}. \quad (37a)$$

At the critical point, p_c should satisfy $\partial p / \partial Q|_{t_c} = 0$ and $\partial^2 p / \partial Q^2|_{t_c} = 0$, then from equation (37a) we have

$$t_c = -(6 - 4\sqrt{2}) \left[k_{f1} \left(\frac{\sigma}{b_f} \right)^{*12} - k_{f2} \left(\frac{\sigma}{b_f} \right)^{*6} \right] \\ p_c = -0.1603 \times \left[k_{f1} \left(\frac{\sigma}{b_f} \right)^{*12} - k_{f2} \left(\frac{\sigma}{b_f} \right)^{*6} \right] / \left\{ [1 + C(x^* + 2y^*)] \left(\frac{b_f}{\sigma} \right)^{*2} \right\} \\ Q_c = 2 - \sqrt{2} \quad (46)$$

where t_c , p_c and Q_c are the temperature, pressure and molecular fraction at the critical point respectively. In equation (46), if we take the values of parameters $(b_f/\sigma)^*$, x^* and y^* , which are close to the higher temperature in table 2, then we can get the position of the critical point, which is about $t_c \approx 0.99$ and $p_c \approx 0.33$.

In order to describe clearly the critical state of the system, we study the isothermal line of the system. Using equation (35) and $A = (\partial G^* / \partial P)_T = (A_0 / N\varepsilon) (\partial G^* / \partial p)_t$, the system

area A is

$$A = A_0[1 + C(x^* + 2y^*)] \left(\frac{b_f}{\sigma}\right)^{*2} / Q. \quad (47)$$

Thus we can obtain an equation of the state of the liquid (or gas) phase system by equation (37a) and (47), that is

$$p \left[k_{f1}^* \left(\frac{\sigma}{b_f}\right)^{*12} - k_{f2}^* \left(\frac{\sigma}{b_f}\right)^{*6} \right] [1 + C(x^* + 2y^*)] \left(\frac{b_f}{\sigma}\right)^{*2} / \tilde{A}^2 + t / \tilde{A} - t \ln \left\{ 1 - [1 + C(x^* + 2y^*)] \left(\frac{b_f}{\sigma}\right)^{*2} / \tilde{A} \right\} / [1 + C(x^* + 2y^*)] \left(\frac{b_f}{\sigma}\right)^{*2} \quad (48)$$

where

$$\tilde{A} = A/A_0.$$

If we fix the normalized temperature t , using equation (48), we can obtain a series of isothermal lines of $p \sim \tilde{A}$, as shown in figure 4. From figure 4, we find that when $t > t_c$, a limit point in those curves does not exist; if $p > 0$, then we find that when $t < t_c$ there are a minimum point and a maximum point in those curves; and when $t = t_c$, we find a plot of a line approximate to the horizon at $p = p_c \approx 0.33$.

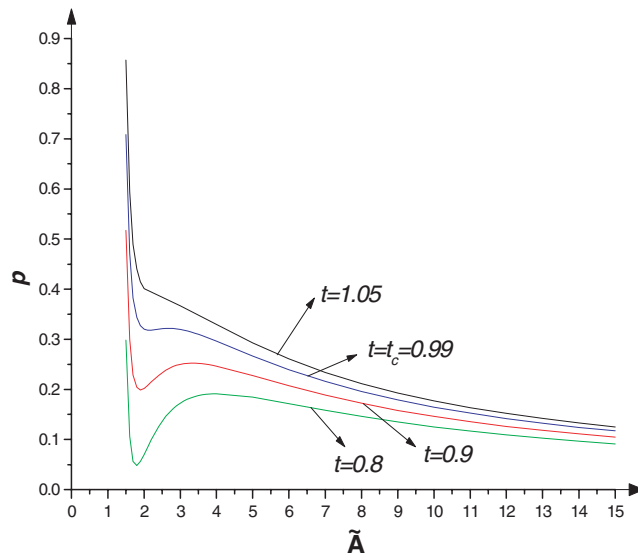


Figure 4. The relation between p and \tilde{A} : the isothermal lines correspond to four different fixed t 's.

5. Discussion

- (1) The L-J potential is usually used for the interaction between inert gas crystals, so introducing an L-J potential into the Collins model is a convenient method in order to compare our results with the experimental results of an inert gas crystal. Our present work gives the triple point at about $t_t \approx 0.38$, $p_t \approx 0.009$. According to [7], the triple point temperature of Xe is $T = 98.2$ K, if we let $\varepsilon = 0.020$ eV [12], then $t_t = 0.423$.

Again, according to [7], the triple point temperature of Ar is about $T = 48$ K, if we let $\varepsilon = 0.0104$ eV [12], then $t_t = 0.398$. We can, therefore, see that our results agree well with experimental results. Furthermore, the Monte Carlo computer simulation result is $t_t = 0.415$, $p_t = 0.0056$ [8], with which our results also agree quite well.

- (2) From thermodynamics, the critical coefficient of a 2D system is

$$K_K = NK_B T_c / P_c A_c = t_c / p_c \tilde{A}_c$$

where $\tilde{A}_c = A_c/A_0 + [1 + C(x^* + 2y^*)](b_f/\sigma)^2/Q_c$. Using equation (46), we get $K_K = 1.266$ or $1/K_K = 0.79$. The experimental results of the inert gas are [16]: for He, $1/K_K = 0.302$; for Ne, $1/K_K = 0.311$; for Ar, $1/K_K = 0.291$; for Kr, $1/K_K = 0.288$; for Xe, $1/K_K = 0.287$. So we can see that our results agree with the experimental values in the order of magnitude although a difference does exist.

- (3) From figure 3 we can see that the critical point (\blacktriangledown) does not fit with the vaporization line. The reason is that the critical point (\blacktriangledown) is obtained from equation (46), which is not an approximate result, and the vaporization line is obtained from equations (44) and (45) which are first-order approximate results. With the increase in the temperature, the first-order approximate condition, i.e. equation (38), cannot be satisfied so well. So the critical point (\blacktriangledown) deviates slightly from the vaporization line.
- (4) From table 2 we can see that y^* is about 0.008, which means the 4-atom percentage is very small, only about 0.8%. Whether the existence of a 4-atom structure will influence the phase diagram, the triple point and the critical point shall be discussed in another paper.

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