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# The two-dimensional solid–liquid phase transition in the Collins liquid model

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**Abstract.** The Lennard-Jones interaction has been introduced into the Collins mixed lattice for two-dimensional (2D) liquids. By means of rigorous calculation of the total potential and the free area, the Gibbs functions for 2D liquids and solids have been derived. The melting line obtained from the phase transition equation agrees quite well with the results of recent computer simulation experiments. The reduced triple-point temperature $T_t^*$ of 0.438 obtained agrees with the data measured in experiments on some inert-gas monolayers adsorbed on graphite as well as in computer simulation experiments.

## 1. Introduction

Melting in two dimensions (2D) has been a recent subject of interest. Theoretical interest in the problem of long-range crystalline order of lower-dimensional systems extends back many years. In the mid-1930s the lack of long-range translational order in 2D solids was demonstrated [1, 2]. However, as pointed out in [3], the weak logarithmic dependence on size allows a finite sample to be ordered over a finite range of temperatures. Thus, the theory does not exclude the solid phase of laboratory-sized monolayer films and is therefore in accord with experimental solid-like heat capacities [4]. A detailed theory of melting in 2D has been put forward in [5–7]. It was proposed that a solid–liquid transition in 2D is mediated by a new phase called a 'hexactic phase' and the melting transition can be continuous. However, some experimental results and computer simulations still strongly indicate that both types of transition may occur in the same system [8]. The melting of Ar, Kr and Xe submonolayers was examined in 1982 [9] by synchrotron x-ray diffraction and a set of reliable triple-point temperatures were obtained. The comparison of the three systems under the same experimental conditions is a significant advance in clarifying the complexities of substrate-influenced melting. The interpretation of the results of these investigations have led to controversies regarding the nature of the transition and the existence of a hexactic phase. Some workers suggest a possible hexactic phase at moderate densities, but a first-order transition at high densities [10]. Both the experimental and the theoretical situations are, at present, quite mysterious and challenging.

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In this paper, we present a simple geometric theory of 2D melting based on the Collins model of liquids. We have adopted the Lennard-Jones (12,6) potential to represent the interactions between molecules. The Collins liquid model is a spatially random lattice in 2D constructed by closely packing the plane with equilateral triangles and squares. We called this triangular–square lattice a mixed lattice. Although this theory explores the consequences of a first-order transition directly from the solid to the isotropic liquid, it cannot rule out the possibility of the dislocation-mediated melting in [5–7]. Since the Lennard-Jones potential is a fair approximation to the interaction of inert-gas atoms, our results will give qualitative accounts of the phase diagrams for physisorbed inert gases without registry effects. The comparison with the experimental triple point and melting line will be conducive to better understanding of the geometric configurations of molecules in 2D liquids and to further evaluation of the statistical geometric theory of melting. The mixed lattice model was studied in [11, 12], but the discussions are all limited to the square well pair potential which works only between nearest neighbours; thus the results have only qualitative meaning and cannot be compared with real systems.

Our model of liquids is explained in § 2. Since a detailed discussion of the Collins model in the study of the melting of 2D hard disc and square well systems was presented in [13], the present paper will only give a brief introduction. In § 3 the total potential energy of the mixed lattice is accurately evaluated by the numerical method in § 4. The solid–liquid transition and the melting line are obtained in § 5, and § 6 is devoted to a summary and discussion.

## 2. The Collins mixed lattice model

The aim of the physics of liquids is to understand why particular phases are stable in particular ranges of temperature and density. The most severe difficulties in the theory of liquids arise because there is no obvious way of reducing the complex many-body problem posed by the motion of the molecules to a one-body problem, analogous to the phonon analysis of motions in crystals or to the virial series for dilute gases. Among the earliest theories of liquids were 'cell' or 'free-volume' theories which were based on the intuitive idea that a molecule in a liquid is essentially confined to a cell or cage formed by its neighbours. However, this cell theory [14] appears to describe solids and not liquids, since the theory uses essentially the Einstein model with full correction for anharmonicity. In an actual liquid, long-range order is absent in spite of the fact that its density is relatively high close to the corresponding crystal density. In contrast, it retains short-range order which is quite similar to that of the crystal. In 1964 a mixed lattice model of liquids was proposed [15]. This is a close-packed assembly of squares and triangles (figure 1). If we link the nearest neighbours by bonds, we obtain a planar network consisting of equilateral triangles, squares and pentagons. When all polygons are triangles, the lattice is a regular triangular lattice which corresponds to the crystalline state. When the configuration becomes more loosely packed and all polygons higher than pentagons are neglected, we obtain a triangular–square lattice which corresponds to the liquid state. The important parameter for describing the mixed lattice is the ratio of the number of triangles to the number of squares. When this ratio takes a certain intermediate value, the lattice becomes highly random without any long-range order but the short-range order is always preserved in the sense that all bonds have equal lengths. We regard such a state as a model for 2D liquids. Therefore, this simple model can properly represent the most prominent character of liquid structure.

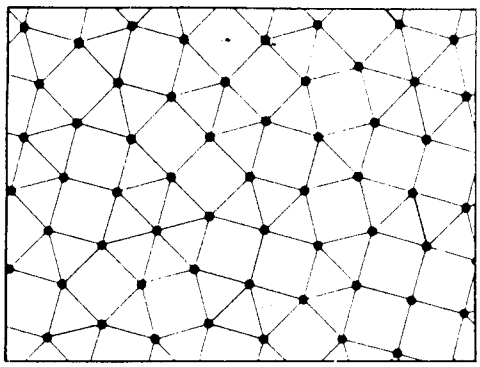

**Figure 1.** The Collins mixed lattice model of liquid.

In the Collins mixed lattice, possible local configurations of triangles and squares around a vertex are shown in figure 2. There are four types of possible configuration: A, B, C and H. Let the numbers of these four types of lattice point be denoted by $N_i$ ($i \equiv$ A, B, C, H), then

$$\sum_i N_i = N = \text{constant}. \tag{1}$$

The partition function $Z(N_A, N_B, N_C, N_H, T)$ of the system can be written as

$$Z = W \prod_i \lambda^{-2N_i} \exp\left(-\frac{N_i \varepsilon_0(i)}{2kT}\right) [a_f(i)]^{N_i} \tag{2}$$

where $\varepsilon_0(i)$ is the potential energy of one molecule located at a lattice point of type i with the remaining $N - 1$ molecules of the system fixed at their lattice points, $a_f(i)$ is the free area of type i, $\lambda = h/(2mkT)^{1/2}$ is the thermodynamic wavelength and $W$ is the number of all different configurations formed under constant $N_i$.

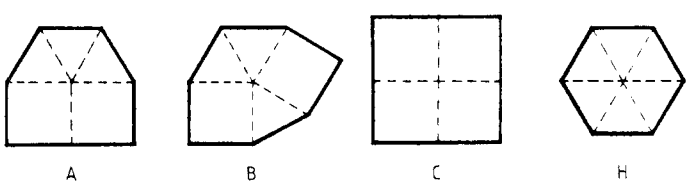


**Figure 2.** Local configurations of 2D liquids.

Apparently, when writing the partition function of the system, we adopt a method similar to that used for dealing with the mixed solutions [16]. Namely, we consider that the four different types of lattice point in the Collins mixed lattice correspond to the molecules of different components in the mixed solutions. Denote $U_0$ as the total potential of the system when every molecule is located at its lattice point; then

$$U_0 = \tfrac{1}{2} \sum_i N_i \varepsilon_0(i) \tag{3}$$

where the factor $\frac{1}{2}$ is in order to avoid double counting. Substitute (3) into (2); then

$$Z = W\lambda^{-2N} \exp\left(-\frac{U_0}{kT}\right) \prod_{\mathrm{i}} [a_{\mathrm{f}}(\mathrm{i})]^{N_{\mathrm{i}}}. \tag{4}$$

Here, we regard $U_0$ in each of $W$ different configurations as the same. This assumption is correct for the mixed lattice when the interactions are only between the nearest and the next-nearest neighbours. The Lennard-Jones potential can roughly satisfy this condition because the interactions decrease rapidly as the separation increases. In § 3, we shall see that the number of those pairs of molecules which have distances shorter than $\sqrt{7}b$ (where $b$ is the lattice constant) depend on the variables $N_{\mathrm{i}}$ only, in spite of the arrangement of the four types of lattice point. Hence the $U_0$ in each of $W$ different configurations are approximately equal in fact.

In particular, in order to pack closely the plane with triangles and squares the number $W(N_{\mathrm{A}}, N_{\mathrm{B}}, N_{\mathrm{C}}, N_{\mathrm{H}}, T)$ of configurations is related not only to the number of permutations $N!/N_{\mathrm{A}}!N_{\mathrm{B}}!N_{\mathrm{C}}!N_{\mathrm{H}}!$, but also to the geometrical constraint conditions; so

$$W = (N!/N_{\mathrm{A}}!N_{\mathrm{B}}!N_{\mathrm{C}}!N_{\mathrm{H}}!)F_{\mathrm{c}}(N_{\mathrm{A}}, N_{\mathrm{B}}, N_{\mathrm{C}}, N_{\mathrm{H}}). \tag{5}$$

The constraint factor $F_{\mathrm{c}}$ imposes a severe geometrical restriction over the whole system. It has been discussed in detail and the rigorous expression of $F_{\mathrm{c}}$ has been derived in [13].

## 3. Total potential of the 2D Lennard-Jones system

The geometrical constraint relation in the Collins mixed lattice makes it impossible for different types of lattice point to exchange without affecting other neighbours; so the total number $W$ of configurations is always smaller than the number of ways in which $N$ points can be arranged in a plane under constant $N_{\mathrm{i}}$ ($\mathrm{i} \equiv \mathrm{A, B, C, H}$). This means that there is a certain correlation or order of the molecules in the system within a distance greater than the lattice constant $b$. Hence, for the Lennard-Jones potential, it is possible to calculate the total potential of the system with good accuracy.

If we take account of only molecular pairwise interactions, the total potential of the system can be written as

$$U_0(\boldsymbol{R}_1, \boldsymbol{R}_2, \ldots, \boldsymbol{R}_N) = \sum_j N_j \Phi(r_j) \tag{6}$$

where $\boldsymbol{R}_k$ ($k = 1, 2, \ldots, N$) is the position of each lattice point, $N_j$ is the number of molecular pairs which have distance $r_j$ from each other, and

$$\Phi(r) = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6] \tag{7}$$

is the Lennard-Jones potential, in which $-\varepsilon$ is the minimum of the potential and $\sigma$ is the distance between the two molecules at zero potential.

As the Lennard-Jones interaction approaches zero as $1/r^6$ at large distances, the contribution of those molecular pairs with a large distance to the total potential can be neglected, so that we can choose an appropriate truncated distance as $r_{\mathrm{c}} = \sqrt{7}b \simeq 2.6b$ in the calculation of the total potential $U_0$. In this case, $\Phi(r_{\mathrm{c}})/\Phi(b) \simeq 0.5\%$. In the Collins mixed lattice, there are only seven types of molecular pairs distance 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 $\sqrt{(4+\sqrt{3})}b$. All the seven types of molecular pair are included in the four types of local configuration: A, B, C, H. Hence, all the numbers $N_j$ ($j = 1, 2, \ldots, 7$) are related only to $N_{\mathrm{i}}$ ($\mathrm{i} \equiv \mathrm{A, B, C,}$

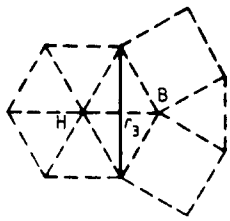


**Figure 3.** The molecular pairs in local configurations.

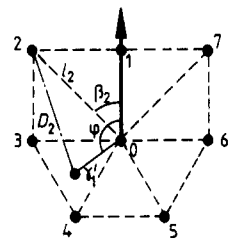


**Figure 4.** Cell geometry of the Collins mixed lattice.

H), but not to the way in which the four types of lattice point are arranged in the configurations.

Take the molecular pair with distance $r_3 = \sqrt{3}b$ for example; local configurations of types A, B, C and H contain 2, 1, 0 and 6 such molecular pairs, respectively. Considering that such a molecular pair is counted twice in two local configurations (figure 3), the total number $N_3$ of these pairs in a configuration is

$$N_3 = \tfrac{1}{2}(2N_A + N_B + 6N_H) = \tfrac{1}{2}(2n_A + n_B + 6n_H)N$$

where $n_i = N_i/N$ (i ≡ A, B, C, H). Using the same method, we can derive the numbers of the other six types of molecular pair; the results are shown in table 1.

**Table 1.** The numbers of the molecular pairs in the Collins mixed lattice.

| $j$ | $r_j$ | $N_j$ |
|---|---|---|
| 1 | $b$ | $(5n_A + 5n_B + 4n_C + 6n_H)N/2$ |
| 2 | $\sqrt{2}b$ | $(n_A + n_B + 2n_C)N$ |
| 3 | $\sqrt{3}b$ | $(2n_A + n_B + 6n_H)N/2$ |
| 4 | $\sqrt{(2+\sqrt{3})}b$ | $(2n_A + 4n_B)N$ |
| 5 | $2b$ | $(n_A + 2n_C + 3n_H)N$ |
| 6 | $\sqrt{5}b$ | $(n_A + 4n_C)N$ |
| 7 | $\sqrt{(4+\sqrt{3})}b$ | $(2n_A + 2n_B)N$ |

Substituting $N_j$ and $r_j$ ($j = 1, 2, \ldots, 7$) into (6) and considering $n_A + n_B + n_c + n_H = 1$, we find the total potential

$$U_0 = \varepsilon[k_{f1}(\sigma/r)^{12} - k_{f2}(\sigma/r)^6]N \tag{8}$$

where the coefficients $k_{f1}$ and $k_{f2}$ are

$$\begin{aligned} k_{f1} &= 12.0194 - 1.9470n_A - 1.9484n_B - 3.8914n_C \\ k_{f2} &= 12.6319 - 1.7782n_A - 1.7926n_B - 3.3789n_C. \end{aligned} \tag{9}$$

For a 2D solid, let $n_A = n_B = n_C = 0$; we can obtain the total potential of the system under the same truncated distance $r_c = \sqrt{7}b$; the corresponding coefficients are

$$k_{s1} = 12.0194 \qquad k_{s2} = 12.6319. \tag{9'}$$

As the structure of a 2D solid is a regular triangular lattice, let the truncated distance $r_c \to \infty$; we can accurately calculate the total potential. As a result, the coefficients $k_{s1}$

and $k_{s2}$ are 12.0196 and 12.7460, respectively. However, when we calculate the melting transition, only the difference in the total potential between the solid and liquid states ($\Delta U_0 = U_{0s} - U_{0f}$) appears in the phase transition equation. Hence, if we choose the same truncated distance $r_c$ for both solid and liquid states, the errors will be partially counteracted, and the result will be more accurate.

## 4. Calculation of the free areas

Corresponding to the four types of lattice point in the Collins model, there are four types of free area; their general expression is

$$a_f(\mathrm{i}) = \int_\Delta \exp\left(-\frac{\Delta V_\mathrm{i}(\boldsymbol{r})}{kT}\right) \mathrm{d}\boldsymbol{r} \qquad (\mathrm{i} \equiv \mathrm{A, B, C, H}) \tag{10}$$

where $\Delta V_\mathrm{i}(\boldsymbol{r})$ is the additional potential energy due to a central molecule which is at a distance $\boldsymbol{r}$ from the centre of the cell of type i. Like the cell theory in [14], the neighbours of the molecule are at the centres of their cells when $\Delta V_\mathrm{i}(\boldsymbol{r})$ is calculated.

Suppose a molecule within a cell of type i has $M_\mathrm{i}$ nearest and next-nearest neighbours (for type A, $M_\mathrm{A} = 7$ (figure 4)), the distance between the $k$th molecule of the $M_\mathrm{i}$ molecules and the central lattice point is $\xi_k = Q_k b$ (for type A, $Q_1 = Q_3 = Q_4 = Q_5 = Q_6 = 1$ and $Q_2 = Q_7 = \sqrt{2}$). If we set up a polar coordinate system by taking the direction from the central point to the first neighbouring molecule as the polar axis, then the polar angle of the connecting line from the central point to the $k$th neighbouring molecule is $\beta_k \pi$ (for type A, $\beta_1 = 0$, $\beta_2 = \frac{1}{4}$, $\beta_3 = \frac{1}{2}$, $\beta_4 = \frac{5}{6}$, $\beta_5 = \frac{7}{6}$, $\beta_6 = \frac{3}{2}$ and $\beta_7 = \frac{7}{4}$). When the molecule has coordinates $(r, \varphi)$, the distance between it and the $k$th neighbouring molecule can be derived from the cosine law:

$$D_k = [r^2 + \xi_k^2 - 2r\xi_k \cos(\varphi - \beta_k \pi)]^{1/2}. \tag{11}$$

Then the additional potential energy $\Delta V_\mathrm{i}(\boldsymbol{r})$ becomes

$$\begin{aligned}\Delta V_\mathrm{i}(\boldsymbol{r}) &= \sum_{k=1}^{M_\mathrm{i}} \Phi(D_k) - \sum_{k=1}^{M_\mathrm{i}} \Phi(\xi_k) \\ &= 4\varepsilon \sum_{k=1}^{M_\mathrm{i}} \left\{\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] - \left[\left(\frac{\sigma}{Q_k b}\right)^{12} - \left(\frac{\sigma}{Q_k b}\right)^{6}\right]\right\}.\end{aligned} \tag{12}$$

The values of $M_\mathrm{i}$, $Q_k$ and $\beta_k$ corresponding to the four local configurations are shown in table 2.

Substituting (12) into (10), we obtain the $a_f(\mathrm{i})$ ($\mathrm{i} \equiv \mathrm{A, B, C, H}$). The integration region $\Delta$ in (10) is the cell of each 2D local configuration. The integrand decreases rapidly

**Table 2.** Geometric parameters in calculation of free areas.

| i | $M_\mathrm{i}$ | $Q_k (k = 1, \ldots, M_\mathrm{i})$ | $\beta_k (k = 1, \ldots, M_\mathrm{i})$ |
|---|---|---|---|
| A | 7 | $1, \sqrt{2}, 1, 1, 1, 1, \sqrt{2}$ | $0, \frac{1}{4}, \frac{1}{2}, \frac{5}{6}, \frac{7}{6}, \frac{3}{2}, \frac{7}{4}$ |
| B | 7 | $1, 1, \sqrt{2}, 1, 1, \sqrt{2}, 1$ | $0, \frac{1}{3}, \frac{7}{12}, \frac{5}{6}, \frac{7}{6}, \frac{17}{12}, \frac{5}{3}$ |
| C | 8 | $1, \sqrt{2}, 1, \sqrt{2}, 1, \sqrt{2}, 1, \sqrt{2}$ | $0, \frac{1}{4}, \frac{1}{2}, \frac{3}{4}, 1, \frac{5}{4}, \frac{3}{2}, \frac{7}{4}$ |
| H | 6 | $1, 1, 1, 1, 1, 1$ | $0, \frac{1}{3}, \frac{2}{3}, 1, \frac{4}{3}, \frac{5}{3}$ |

with increasing distance $r$; so in actual calculations we choose a suitable value as the integral's upper limit of $r$ to simplify the calculation without significant errors.

In general, $\Delta V_i(\boldsymbol{r})$ in equation (10) is related to the direction $\varphi$ of $\boldsymbol{r}$. It is impossible to calculate by an analytical method, and we are obliged to calculate it by a numerical method.

In a study of three-dimensional (3D) systems [16], an average potential was introduced to simplify similar integrals. Here we can also define an average potential for 2D systems in the same way as

$$\overline{\Delta V_i(\boldsymbol{r})} = c_{1i}\left(\frac{1}{2\pi}\int_0^{2\pi} \Phi(|\boldsymbol{r}-\boldsymbol{b}|)\,\mathrm{d}\varphi - \Phi(b)\right) \tag{13}$$

where $c_{1i}$ is the number of nearest neighbours of a lattice point of type i. Substituting the Lennard-Jones interaction into equation (13), we have

$$\overline{\Delta V_i(\boldsymbol{r})}/c_{1i} = 4\varepsilon[(\sigma/b)^{12}L(r^2/b^2) - (\sigma/b)^6 M(r^2/b^2)] \tag{14}$$

where

$$L(x) = (1 + 45x + 100x^2 + 100x^3 + 25x^4 + x^5)/(1-x)^{11} - 1 \tag{15}$$

$$M(x) = (1 + 4x + x^2)/(1-x)^5 - 1. \tag{16}$$

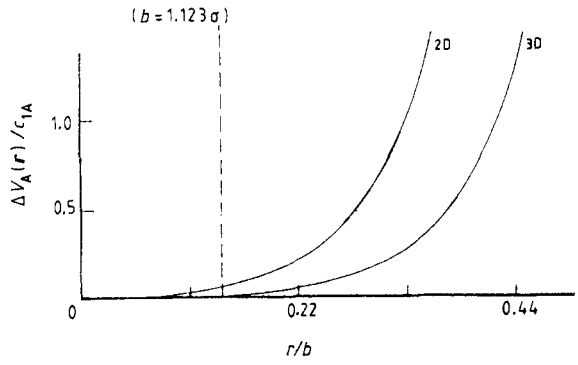


**Figure 5.** Average potential of 2D and 3D systems.

These two expressions are obviously different from the two corresponding expressions for 3D systems in their coefficients and degrees of the polynomials. In figure 5 the $\overline{\Delta V_i(\boldsymbol{r})}/c_{1i}$ in 2D systems is compared with that in 3D systems. We can see that the increase in $\overline{\Delta V_i(\boldsymbol{r})}/c_{1i}$ in 2D systems with increase in $r$ is faster than that in 3D systems.

Obviously, in the average potential defined by equation (13), we only take account of the nearest-neighbour interactions. If we also take account of the next-nearest-neighbour interactions, the average potential is

$$\overline{\Delta V_i(\boldsymbol{r})} = c_{1i}\left(\frac{1}{2\pi}\int_0^{2\pi} \Phi(|\boldsymbol{r}-\boldsymbol{b}|)\,\mathrm{d}\varphi - \Phi(b)\right) + c_{2i}\left(\frac{1}{2\pi}\int_0^{2\pi} \Phi(|\boldsymbol{r}-\sqrt{2}\boldsymbol{b}|)\,\mathrm{d}\varphi - \Phi(\sqrt{2}b)\right)$$

$$= c_{1i}\left[\frac{1}{2\pi}\int_0^{2\pi}\left(\Phi(|\boldsymbol{r}-\boldsymbol{b}|)+\frac{c_{2i}}{c_{1i}}\Phi(|\boldsymbol{r}-\sqrt{2}\boldsymbol{b}|)\right)\mathrm{d}\varphi\right.$$
$$\left.-\left(\Phi(b)+\frac{c_{2i}}{c_{1i}}\Phi(\sqrt{2}b)\right)\right] \tag{17}$$

where the $c_{2i}$ is the number of the next-nearest neighbours of a lattice point of type i. If we also take account of more interactions (up to $r = \sqrt{7}b$), it becomes

$$\overline{\Delta V_i(\boldsymbol{r})} = c_{1i}\left(\frac{1}{2\pi}\int_0^{2\pi}\Phi'(|\boldsymbol{r}-\boldsymbol{b}|)\,\mathrm{d}\varphi - \Phi'(b)\right) \tag{17$'$}$$

where

$$\Phi'(r) = 4\varepsilon[k'_{f1}(\sigma/b)^{12} - k'_{f2}(\sigma/b)^6]$$

and

$$k'_{f1} = k_{f1}/12 \qquad k'_{f2} = k_{f2}/12.$$

Although by using the $\Delta V_i(\boldsymbol{r})$ defined by equation (13), (17) or (17′) the approximate value of free area in equation (10) can be obtained more easily, yet how approximate it can be remains to be studied further. In this paper, we still carry out the numerical integration in a plane area, substituting equations (11) and (12) into equation (10). It is apparent that this calculation takes account of only the nearest- and next-nearest-neighbour interactions.

## 5. Solid–liquid phase transition and melting line

Where the total potential $U_0$, the free area $a_f(\mathrm{i})$ ($\mathrm{i} \equiv \mathrm{A, B, C, H}$) and the constraint factor $F_c$ obtained in [13] are substituted into equation (4), the partition function for a liquid is

$$Z = W\lambda^{-2N}\exp\left\{-\frac{N\varepsilon}{kT}\left[k_{f1}\left(\frac{\sigma}{b}\right)^{12} - k_{f2}\left(\frac{\sigma}{b}\right)^6\right]\right\}\prod_i [a_f(\mathrm{i})]^{N_i}$$
$$= \frac{N!}{N_A!N_B!N_C!N_H!}(n_A+n_B)^{N_A+2N_B}(n_A+n_C)^{N_A/2+2N_C}$$
$$\times (n_A+n_B+n_C)^{(N_A+N_b)/2+N_C}(n_A+n_B+n_H)^{N_A+N_B/2+3N_H}$$
$$\times \lambda^{-2N}\exp\left\{-\frac{N\varepsilon}{kT}\left[k_{f1}\left(\frac{\sigma}{b}\right)^{12} - k_{f2}\left(\frac{\sigma}{b}\right)^6\right]\right\}\times\prod_i [a_f(\mathrm{i})]^{N_i}. \tag{18}$$

From thermodynamic relations the equation of state and the Gibbs function for a liquid can be obtained:

$$P = -(\partial F/\partial A)_{T,N} = kT[(\partial/\partial b)\ln Z)\Big]_{T,N}(\partial b/\partial A)_N \tag{19}$$

$$G = F + PA = -kT\ln Z + PA. \tag{20}$$

The relation between total area $A$ and lattice constant $b$ for a liquid can be derived directly from the geometrical relation [13]

$$A = A_0(b/\sigma)^2\{1 + [(2\sqrt{3}-3)/6](n_A + n_B + 2n_C)\} \tag{21}$$

where $A_0 = (\sqrt{3}/2)N\sigma^2$ is the total area of the triangular lattice for close packing. When equations (18) and (21) and the thermodynamic wavelength are substituted into equation (20), and if $n_A + n_B + n_C + n_H = 1$, the complete expression for the Gibbs free energy for a liquid is

$$\begin{aligned}\frac{G_f}{NkT} = {} & n_A \ln n_A + n_B \ln n_B + n_C \ln n_C + (1 - n_A - n_B - n_C)\ln(1 - n_A - n_B - n_C) \\ & - (n_A + 2n_B)\ln(n_A + n_B) - \tfrac{1}{2}(n_A + 4n_C)\ln(n_A + n_C) \\ & - \tfrac{1}{2}(n_A + n_B + 2n_C)\ln(n_A + n_B + n_C) - (3 - 2n_A - \tfrac{5}{2}n_B - 3n_C) \\ & \times \ln(1 - n_C) + \ln\left(\frac{h^2}{2\pi mkT}\right) + \frac{\varepsilon}{kT}\left[k_{f1}\left(\frac{\sigma}{b_f}\right)^{12} - k_{f2}\left(\frac{\sigma}{b_f}\right)^{6}\right] \\ & - \sum_i n_i \ln[a_f(i)] \times \frac{PA_0}{NkT}\left(\frac{b_f}{\sigma}\right)^2 \left[1 - \frac{2\sqrt{3} - 3}{6}(n_A + n_B + 2n_C)\right]. \end{aligned} \tag{22}$$

For a solid, $W = 1$, and $N_A = N_B = N_C = 0$, $N_H = N$; by substituting these into the above expressions, we can obtain the corresponding expressions for a solid. The Gibbs free energy is

$$\begin{aligned} G_s/NkT = {} & \ln(h^2/2\pi mkT) + (\varepsilon/kT)[k_{s1}(\sigma/b_s)^{12} - k_{s2}(\sigma/b_s)^6] - \ln[a_f(H)] \\ & + (PA_0/NkT)(b_s/\sigma)^2. \end{aligned} \tag{23}$$

In equations (22) and (23) the $b_f$ and $b_s$ are the lattice constants for a liquid and a solid, respectively, and $a_f(H)$ is just the free area of a regular triangular lattice.

By using the stability conditions

$$\begin{aligned} &\partial G_f/\partial n_i = 0 \qquad \partial^2 G_f/\partial n_i^2 > 0 \qquad (i = A, B, C) \\ &\partial G_j/\partial b_j = 0 \qquad \partial^2 G_j/\partial b_j^2 > 0 \qquad (j = f, s). \end{aligned} \tag{24}$$

the value of $n_i$ ($i \equiv A, B, C, H$), and the lattice constants $b_f$ and $b_s$ can be determined for different pairs of $(T, P)$ after the minimisation of $G$.

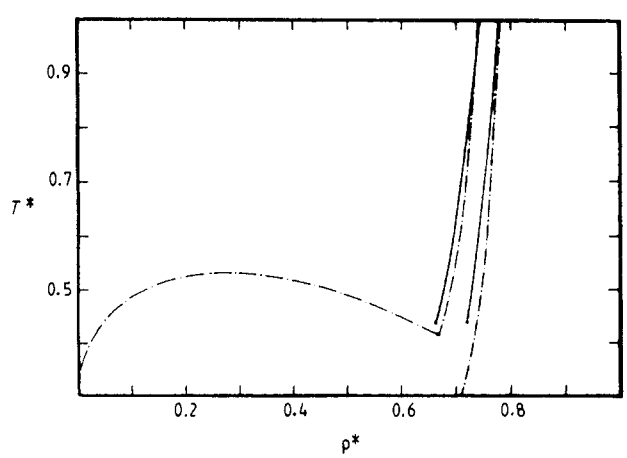


**Figure 6.** Melting line of Lennard-Jones system.

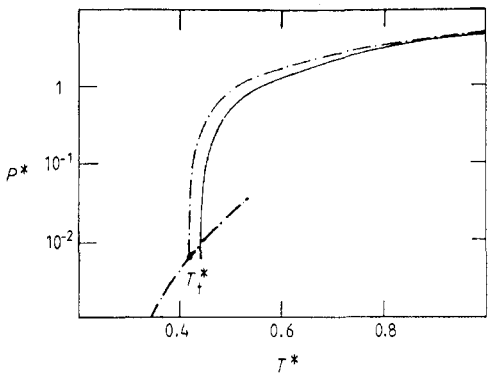


**Figure 7.** Reduce triple-point temperature of 2D Lennard-Jones system.

At the solid–liquid phase transition, the Gibbs free energies for different phases must satisfy the phase transition equation

$$G_f = G_s. \tag{25}$$

On substitution of equations (23) and (24) into the phase transition equation (25), the melting line $P = P(T)$ can be solved. Let $P = 0$ at the melting line; the approximate value of triple-point temperature can be determined.

The results of numerical calculation are shown in figures 6 and 7 and are listed in table 3. The results of the computer simulation experiments [17, 18] for the 2D Lennard-Jones system are also shown for comparison. In all these cases, $T^* = kT/\varepsilon$ is the reduced

**Table 3.** Numerical results of the melting of a 2D Lennard-Jones system. The values in parentheses are the results of the computer simulation experiments for a 2D Lennard-Jones system.

| $T^*$ | $P^* = PA_0/N\varepsilon$ | $\rho_f^* = \rho/\rho_0$ | $\rho_s^* = \rho/\rho_0$ | $\Delta(S/NK)$ | $\Delta(PA/NkT)$ | $\Delta(U/NkT)$ |
|---|---|---|---|---|---|---|
| 1.00 | 4.87 | 0.744 (0.741) | 0.780 (0.782) | 0.612 | 0.305 | 0.307 |
| 0.70 | 2.10 | 0.710 (0.718) | 0.751 (0.762) | 0.672 | 0.230 | 0.441 |
| 0.55 | 0.84 | 0.687 (0.694) | 0.734 (0.753) | 0.755 | 0.143 | 0.612 |
| 0.45 | 0.09 | 0.667 (0.681) | 0.723 (0.740) | 0.885 | 0.022 | 0.863 |

| $T^*$ | $b_f/\sigma$ | $b_s/\sigma$ | $n_A$ | $n_B$ | $n_C$ | $n_H$ |
|---|---|---|---|---|---|---|
| 1.00 | 1.123 | 1.132 (1.131) | 0.494 | 0.346 | 0.008 | 0.152 |
| 0.70 | 1.150 | 1.154 (1.145) | 0.492 | 0.347 | 0.008 | 0.153 |
| 0.55 | 1.169 | 1.167 (1.152) | 0.491 | 0.348 | 0.009 | 0.152 |
| 0.45 | 1.186 | 1.176 (1.162) | 0.492 | 0.348 | 0.009 | 0.151 |

temperature, $\rho^* = \rho/\rho_0$ is the reduced density and $\rho_0 = 2/\sqrt{3}\sigma^2$ is the density of the close-packed triangular lattice.

From the data in table 3 and figure 6, we can see that the results of the theoretical calculation agree quite well with the computer simulation experiments. At different reduced temperatures, the differences between our calculation and the simulations are less than 2.5% for $b_f$, $b_s$, $\rho_f^*$ and $\rho_s^*$ at the melting transition. From figure 7 the reduced triple-point temperature $T_t^*$ obtained from the calculation is 0.438, which is quite close to the results of synchrotron x-ray diffraction experiments: $T_t^* = 0.41$ for an Ar monolayer, $T_t^* = 0.44$ for an Xe monolayer, and the result of the computer simulation experiments is $T_t^* = 0.415$. From table 3, we can also see that the proportion of the local configuration of type C in a liquid in the melting region is very small. This is consistent with the results of calculations for 2D hard disc and square well systems. Its physical meaning is that, when a liquid is in a melting region, the distribution of molecules must be close to the distribution of molecules in a solid; so the local configuration of type C, the comparatively loose-packed configuration, is relatively rare in a liquid of high density.

## 6. Discussion

The study of the solid–liquid phase transition by the geometric method is an important topic. The present work has proved again that the quantitative results obtained by this statistical geometric theory have a certain reliability.

The heart of the matter is that the assumption of the geometric structure of a liquid in the Collins model is essentially quite close to the real picture of a liquid. First, the Collins model correctly reflects the feature of molecular arrangement in a liquid which has only short-range order but no long-range order. The short-range order is most distinct at $r = b$ and gradually weakens on increase in $r$. For $r > \sqrt{7}b$, the order disappears rapidly. Secondly, under constant $N_i$ ($i \equiv$ A,B, C, H), the Collins model produces many unequal configurations; so it reflects more naturally than other theories do the increase in entropy from solid state to liquid state. Thirdly, in the Collins mixed lattice, local configurations of types A and B appear in the greatest proportion (about 84%). According to the Wigner–Seitz definition [19] of geometric neighbours, these two types of local configuration correspond to the degenerate state with five and seven neighbours. The computer simulation has verified that these local configurations, whose coordination number is not six, are present in 2D systems [20] and appear in large quantities when melting occurs [17]. Therefore we can say that the Collins model also expresses the feature that there are many local configurations with a 'defect' in the coordination number of a liquid.

The results obtained are inconsistent with the dislocation-mediated theory of 2D melting of in [5–7]. Although the local configurations of types A and B can be regarded in a sense as a dislocation core, the existence of a single dislocation is inhibited in our model. The geometrical restriction is so severe in the Collins mixed lattice that a single dislocation necessarily destroys the packing condition and has a cost in energy and enthalpy. It might be interesting to note that such a correlation property of dislocations appears in the form of grain boundaries. Since grain boundaries are composed of dislocations, the crucial difference between a theory involving dislocations and one involving grain boundaries can be traced back to the fact that the potential between dislocations is not of a simple logarithmic form. Indeed, according to grain boundary

melting, it has been argued [21] that a first-order transition should be the rule. Although it is beyond the capacity of the present model calculation to determine whether melting in 2D obeys a first-order or a continuous theory mediated by dislocations, the fact that the present results for the triple point and melting line are consistent with the results of the monolayer experiments and computer simulations suggests that the strong correlation effect leads to the first-order transition in 2D melting. Although very simple, this lattice mixed model contains within it the essential physics of some simple liquids. The use of the model in the 2D system, which consists of polyatomic molecules, is open to further discussion.

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## References

[1] Peierls R E 1934 *Helv. Phys. Acta* **7** 81
[2] Landau L D 1937 *Phys. Z. Sowjetunion* **11** 26
[3] Gunther L 1967 *Phys. Lett.* **25A** 649
[4] Dash J G 1978 *Phys. Rep.* **38** 177
[5] Kosterlitz J M and Thouless D J 1972 *J. Phys. C: Solid State Phys.* **5** L124; 1973 *J. Phys. C: Solid State Phys.* **6** 1181
[6] Halperin B I and Nelson D R 1978 *Phys. Rev. Lett.* **41** 121, 519(E)
[7] Young A P 1979 *Phys. Rev.* B **19** 2457
[8] Heiney P A, Stephens P W, Birgeneau R J, Horn P M and Moncton D E 1983 *Phys. Rev.* B **28** 6416
[9] Mctague J P, Als-Nielsen J, Bohr J and Nielsen M 1982 *Phys. Rev.* B **25** 7765
[10] Tobochnik J and Chester G V 1982 *Phys. Rev.* B **25** 6778
[11] Kawamura H 1980 *Prog. Theor. Phys.* **63** 24
[12] Do Y J, Chen L R and Yen Z T 1982 *J. Phys. C: Solid State Phys.* **15** 3059
[13] Guo Z C and Yi Y M 1987 *Commun. Theor. Phys.* **8** 17
[14] Lennard-Jones J E and Devonshire A F 1937 *Proc. R. Soc.* A **163** 53; 1938 *Proc. R. Soc.* A **165** 1
[15] Collins R 1964 *Proc. Phys. Soc.* **83** 553
[16] Hirschfelder J O, Curtiss C F and Bird R B 1954 *The Molecular Theory of Gases and Liquids* (New York: Wiley)
[17] Abraham F F 1981 *Phys. Rep.* **80** 339
[18] Barker J A, Henderson D and Abraham F F 1981 *Physica* A **106** 226
[19] Mctaque J P, Frekel D and Allen M P 1980 *Ordering in Two Dimensions* ed. S K Sinha (New York: North-Holland)
[20] Phillips J M, Bruch L W and Murphy R D 1981 *J. Chem. Phys.* **75** 5097
[21] Chui S T 1983 *Phys. Rev.* B **28** 178