

Computer-simulation studies of the melting transition of Rb and K intercalated in graphite

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The energy histogram method, introduced by Ferrenberg and Swendsen [Phys. Rev. Lett. **61**, 2635 (1988); **63**, 1195 (1989)], was applied to the constant-temperature molecular-dynamics (MD) simulation of a two-dimensional system with incommensurate structures. We performed MD simulations for the stage-2 graphite intercalation compounds (GIC's) with Rb or K being the intercalants (Rb-GIC's and K-GIC's). The temperature dependence of the specific heat, C_v , is calculated for various sizes up to 864 atoms. The melting temperature was found to be 158 K for Rb-GIC's and 119 K for K-GIC's, which are in agreement with the experimental observations and an earlier MD result for Rb.

I. INTRODUCTION

For over a decade, the melting transitions of two-dimensional (2D) systems have been intensively investigated both experimentally and theoretically, and a valuable review has been given by Strandburg.³ Computer simulation is one of the important techniques used in this field. The determination of the transition temperatures and critical properties at the transition were also done using both Monte Carlo (MC) and molecular-dynamics (MD) simulation techniques, in which a very large amount of computer time is needed for accumulating sufficient configuration information to finally calculate the temperature dependence of the specific heat, and hence to determine the transition temperature and the critical properties. An economical and more efficient method, called the energy histogram method, was, however, introduced by Ferrenberg and Swendsen,^{1,2} and we will briefly describe it below. To our knowledge, this is the first time this method has been applied to a MD study of the 2D melting transition. The real systems we have studied are the stage-2 Rb and K graphite intercalation compounds (GIC's), in which alkali-metal Rb and K atoms are intercalated in graphite forming a sandwichlike structure with a quasi-2D metal sheet between adjacent graphite layers separated by an empty (normal) graphite spacing. A variety of static and dynamic properties of different types of GIC's was extensively studied in the last decade by means of x-ray and neutron-scattering experiments, and most recently reviewed in a volume edited by Zabel and Solin.⁴ The MD simulation method applied to these 2D alkali liquids by Fan and co-workers has been largely successful in reproducing both static and dynamic features of the data.⁵⁻⁹ The determination of the order-disorder phase-transition temperature of GIC's using the MD technique has not been published, although it was

attempted by Fan.⁵ We intend to present this result in this paper and compare it with a more recent constant-temperature MD simulation performed by means of the histogram method. Statistically, the former MD mimics a microcanonical ensemble while the latter, constant-temperature MD, simulates a canonical ensemble. Both methods give rise to consistent results.

Our purpose here is to show the success of the MD simulation and to demonstrate both the efficiency of the energy histogram method and the accuracy of the model used.

II. MODEL POTENTIAL

The input potentials used here are the same as given in Refs. 6-8. The first one is the 2D screened Coulomb pair interaction potential between two alkali-metal atoms with charge Q , at a distance r apart, which was taken from the treatment of Visscher and Falicov¹¹ and adapted for the graphite intercalation compounds by Plischke,¹² and is expressed as

$$V_p(r) = \frac{Q^2}{4\pi\epsilon} \left[\frac{1}{r} - Y(r) \right], \quad (1)$$

where

$$Y(r) = 2 \int_0^\infty dq J_0(qr) D(q) \Phi(q), \quad (1a)$$

with

$$D(q) = \frac{1}{qa_0} \quad (q < 2k_F)$$

or

$$D(q) = \frac{2}{qa_0} [1 - \sqrt{1 - 4k_F^2/q^2}] \quad (q > 2k_F),$$

where $J_0(qr)$ is the zero-order Bessel function, a_0 is the Bohr radius, k_F is the Fermi wave vector, which can be calculated in our 2D system in terms of the areal density of Rb atoms ρ_0 ,^{11,5} and

$$\Phi(q) = \frac{e^{(-qc/2)} \sinh(qc/2)}{\sqrt{A^2(q)-1}} \frac{1+Z(q)}{1-e^{-qc}Z(q)}, \quad (1b)$$

in which

$$Z(q) = A(q) - \sqrt{A^2(q)-1} \quad (1c)$$

and

$$A(q) = \cosh(qc) + D(q) \sinh(qc). \quad (1d)$$

It is obvious that $Y(r)$ represents the screening effects of the donated electron sheets on the interaction potential, while the first term in Eq. (1) is the normal Coulomb potential. The dielectric constant ϵ is the only unknown in this potential and may be treated as an adjustable parameter, along with the in-plane density, to yield a good fit to the position and shape of the first sharp diffraction peak (FSDP) in the liquid structure factor, $S(q)$. ϵ was empirically selected to be 2.35 for Rb and 1.80 for K; Q is the charge transfer to the graphite from the alkali-metal atoms, and $Q=e$, the electron charge, was used for a full charge transfer of one electron. This may not be the correct representation of our real system,⁴ but the flexibility of choice of ϵ can compensate for the error caused by taking $Q=e$. The calculations of the screened part of the interaction pair potential is rather troublesome and time consuming. A Lagrange polynomial was therefore used to simplify our calculations for this potential and the corresponding forces. The details are discussed in Ref. 5.

Another contribution to the single-particle potential is the modulation potential produced by the periodic graphite substrate shown below, which comes from a theory developed by Reiter and Moss:¹⁸

$$V_m(r) = \sum_{\text{HK}} V_{\text{HK}} \exp(i\mathbf{q}_{\text{HK}} \cdot \mathbf{r}), \quad (2)$$

where V_{HK} 's are the Fourier coefficients at the HK graphite reciprocal-lattice rod, which were determined experimentally in the liquid Rb- and K-GIC's state,^{9,10} \mathbf{q}_{HK} is a reciprocal-lattice vector of graphite, and \mathbf{r} is a positional vector of an atom. It was found that only a few coefficients V_{HK} 's are appreciably different from zero. Therefore, this potential is actually a sum of a limited number of sinusoidal functions with the correspondingly nonvanishing strengths of amplitudes. This part of the potential plays an important role in the incommensurate structure at low temperature and in the formation of the variety of complicated diffraction patterns, as shown in Fig. 2.⁸

III. CONSTANT-TEMPERATURE MD AND THE ENERGY HISTOGRAM METHOD

We note that, in the 2D case, $T = E_k/kN$, where k is the Boltzmann constant and N is the total number of atoms in the computer model system, if constant temper-

ature is desired, the kinetic energy of the model system must also be constant. In order to realize this requirement, starting with the Newtonian equations of motion, one can introduce an additional term $-\alpha\mathbf{p}$, where \mathbf{p} is momentum, to the force in the equation of motion below and then use the constraint of $dT/dt=0$ to determine the factor α , as proposed by Hoover, Land, and Morn¹³ and Evans,¹⁴ i.e., we write the equation of motion as

$$\frac{d\mathbf{p}_i}{dt} = -\frac{\partial\phi}{\partial\mathbf{q}_i} - \alpha\mathbf{p}_i, \quad (3)$$

where q_i is the coordinate, p_i is the momentum of the i th particle, and ϕ is the potential. Due to the relation of $E_i = P_i^2/2m_i$, the constraint of $dT/dt=0$ is thereby converted into

$$\sum_i \mathbf{p}_i \frac{d\mathbf{p}_i}{dt} / m_i = 0, \quad (4)$$

which leads to

$$\alpha = - \left[\sum_i \frac{\partial\phi}{\partial\mathbf{q}_i} \mathbf{p}_i / m_i \right] / \left[\sum_i \mathbf{p}_i^2 / m_i \right]. \quad (5)$$

In our case $m_i = m$, the mass of a Rb or K atom. This additional term in the equation of motion is actually a constraint force which ensures the reality of constant temperature in the MD simulation. It is the main difference between the constant-temperature and constant-energy MD simulations.

To determine the transition temperature, one can calculate the constant volume specific heat which must have a turn at the transition point. The location of this turn is just the indication of the transition temperature. From statistics, the specific heat at temperature T can be calculated from the relation of

$$C_v = \frac{(E - \bar{E})^2}{kT^2}, \quad (6)$$

where E is the total energy of the model system and \bar{E} is its average at temperature T . At equilibrium in the model system, one can obtain a set of total energies which are separated by a time interval Δt , approximately equal to a few hundredths of a picosecond (ps). It is then straightforward to make a histogram of energy in terms of the obtained outputs of energy from the simulation. It is apparent that this histogram is proportional to the probability distribution of energy, from which the average of energy \bar{E} can be evaluated for the particular temperature at which the simulation was performed:

$$\bar{E}(T_0) = \sum_{i=1}^n E_i P_{T_0}(E_i), \quad (7)$$

where P_{T_0} is the probability distribution of energy at T_0 . In other words, with the histogram, one has the probability distribution of the total energy and hence can calculate the average energy at a certain temperature. This is just the routine treatment for a canonical ensemble in statistical physics. In principle, the specific heat at different temperatures can be evaluated by repetition of the above

procedures. It is, however, unnecessary to do so on the computer for a variety of temperatures. Instead, one can apply the energy histogram method, introduced by Ferrenberg and Swendsen,^{1,2} to this problem. Since the probability distribution of energy $P_{T'}$ at temperature T' is associated with the distribution P_T at temperature T , by the relation below

$$P_{T'}(E_i) = \frac{P_T(E_i) \exp[E_i(\beta' - \beta)]}{\sum_{j=1}^n P_T(E_j) \exp[E_j(\beta' - \beta)]}, \quad (8)$$

where

$$P_T(E_i) = \frac{N(E_i) \exp(\beta E_i)}{\sum_{j=1}^n N(E_j) \exp(\beta E_j)} \quad (9)$$

and E_i is the total energy of the i th entity with an interval of energy ΔE , and $\beta = 1/kT$, k being the Boltzmann constant, and the symbol of $N(E_i)$ is the number of configurations at the energy interval from E_i to $E_i + \Delta E$ in the phase space, one is thus able to perform the calculations of the average energy \bar{E}' at temperature T' , as shown above, and finally obtain the specific heat C_v at that temperature. In a rather large range of temperatures across the transition, one may then obtain a set of C_v 's at a series of temperatures.

It has been shown^{1,2} that the particular temperature at which the MD simulation is executed to obtain information for the energy histogram should be selected to be as close to the transition temperature as possible. This implies that, if one has no idea in advance about the transition temperature, several trials must be performed to obtain a better result. Also, a small trick must be used while calculating the probabilities, to avoid a tremendously large value due to the possibly very large energy in the exponential. This can be accomplished by multiplying both numerator and denominator of the probability expression above by a factor $\exp(-\beta E_{\max})$, where E_{\max} is the maximum energy involved in the system.

The MD simulation was carried out with several model systems with 54, 96, 150, 216, 294, 384, 486, 600, 726, and 864 Rb atoms, corresponding to 18×18 , 24×24 , 30×30 , 36×36 , 42×42 , 48×48 , 54×54 , 60×60 , 66×66 , and 72×72 unit cells of graphite on the 2D plane. As indicated below in Sec. V, the system with 864 atoms gives rise to the most consistent and satisfactory results for this study. Because of the higher in-plane density of K atoms, we tried the systems with 216, 225, and 235, corresponding to KC_{12} , $\text{KC}_{11.52}$, and $\text{KC}_{11.02}$ atoms for the geometry of 36×36 unit cells, and found that the in-plane density of $\text{KC}_{11.02}$ yielded a better transition temperature which is closer to the experimental value than others (not shown here). This is consistent with our earlier study.⁶ The results of C_v for both Rb and K shown in Fig. 1 are, however, obtained from the 864 model system. The time step Δt for both Rb and K is selected to be equal to 0.01 ps and the temperature fluctuation, within which temperature is not rescaled, is 0.1 K. The final statistical value of

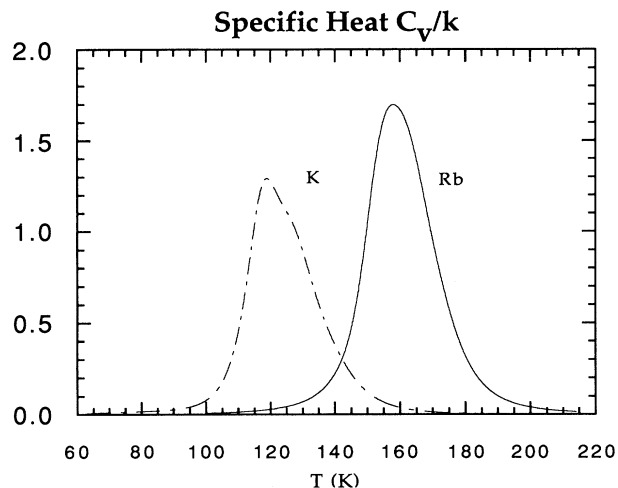


FIG. 1. The temperature dependence of the dimensionless specific heat, C_v/k , where k is the Boltzmann constant, for Rb and K intercalated in graphite, obtained from the constant-temperature MD simulation. The locations of the peaks indicate a transition temperature of 158 and 119 K for rubidium and potassium, respectively.

the specific heat was averaged over 30 000 configurations. It is equivalent to a time elapse of 300 ps.

The plot of C_v vs T is shown in Fig. 1, which clearly indicates the transition temperature of about 158 K for Rb-GIC's and 119 K for K-GIC's. These values are in agreement with the experimental data⁴ and with our previous results from $S(q)$ using the constant energy MD simulation for Rb shown in Figs. 3(a) and 3(b).⁵ Also, they are in accord with the recent result from the extensive constant energy MD simulation of RbC_{12} by Seong *et al.*¹⁷

IV. CONSTANT ENERGY MD SIMULATION

The regular (constant energy) MD simulation was done with a 216-Rb-atom model system in calculating the static structure factor $S(\mathbf{q})$, where \mathbf{q} is the reciprocal-lattice vector, as shown in Fig. 2 and reported before.⁶⁻⁹ We show some earlier results which have not been published and are included in this study in confirmation of the C_v results. The simulational parameters selected were stated elsewhere.⁶⁻⁹ Here we reproduce only one of the plots previously published,⁸ Fig. 2, in order to understand the significance of Fig. 3. This figure is one quarter of a reciprocal-lattice plane centered at the (00) point. The Rb Bragg peaks (the strongest spots on the plot) of (01), (10), and (11) are shown on the corners of the large rhombus and coincide with the graphite peaks which are not shown. Other relatively weak spots are also contributed by Rb atoms, which clearly form a new rhombic crystal structure at low temperature (Fig. 2) and become a blurred or diffuse liquid halo pattern at room temperature.⁹ Due to the modulation of the graphite substrate, each of the spots on the first ring of $S(\mathbf{q})$ are split into two symmetrical spots about the sixfold symmetry axes. The half-angle made by the two radii from point (00) to

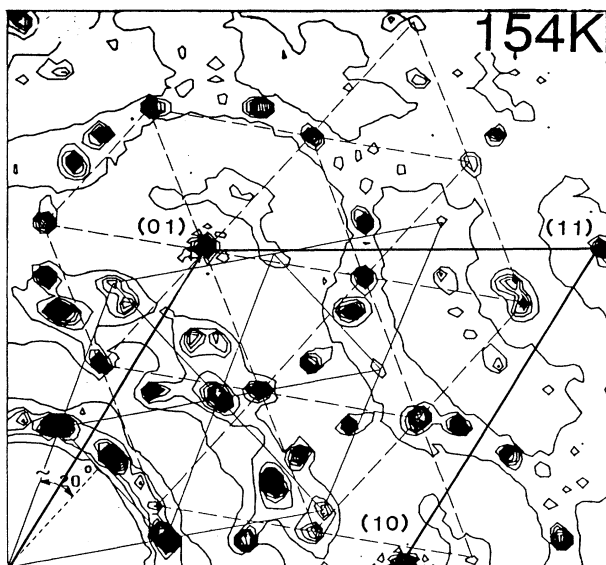


FIG. 2. The anisotropic liquid $S(q)$, where q is a reciprocal-lattice scalar, at 154 K, from Rb as it would appear in a HK section of a graphite sample crystal. Note the sharp Rb contributions at the (10), (01), and (11) graphite Bragg positions, the anisotropic modulated liquid scattering and the development of halos about all (10) positions. [Note also the absence of a halo about (11).] The ripple at the Bragg points is noise.

the split spots is referred to as the rotation angle, which remains constant in either disordered or ordered phase, but jumps to another value across the transition temperature, as has been shown in experiments.^{15,16} It is not difficult to roughly determine the transition temperature by checking the change of the rotation angle. This was done in Ref. 5 and shown in Figs. 3(a) and 3(b), in which one can see that the value of the rotation angle is 15° at temperatures equal to or above 165 and 10° at or below 154 K. This suggests a rough transition temperature of 160 K. A finer result could be obtained if one were to simulate this pattern at temperatures between 165 and 154 K. However, it seems unnecessary to do so because one can do this more precisely and economically with C_v , as stated above. This last result is simply a by-product of the previous simulation work,⁵ in which one was dealing with a microcanonical ensemble where the total energy of the selected model system is conserved according to the classical Newtonian laws, while simultaneously, the kinetic energy, and hence temperature, changes in a relatively large range. In other words, temperature shows a rather large fluctuation about the desired value.

V. DISCUSSION

The results we present here are for the in-plane density of $\sim MC_{12}$, where M represents the alkali-metal atom, either Rb or K. The calculated transition temperatures appear a bit smaller than those from experiments. This seems to be due to the rather low in-plane density of K, as has been noticed in the static structure factor of $S(q)$,⁶ where we have adapted a slightly larger potassium in-

plane density, $KC_{11,02}$, to fit to the position and peak height of FSDP of $S(q)$. We also calculated the temperature dependence of the specific heat, C_v , for this in-plane density on a small model system with 235 K atoms (it would be 216 atoms for the in-plane density of KC_{12}). The plot of C_v vs T indicates a transition temperature of 121 K, closer to the experimental value of 123 K than that of KC_{12} . But for Rb, we did not try a higher in-plane density, because the earlier MD simulation suggested that the in-plane density of RbC_{12} seemed to be a reasonable selection.

Another aspect of our calculations worth mentioning is

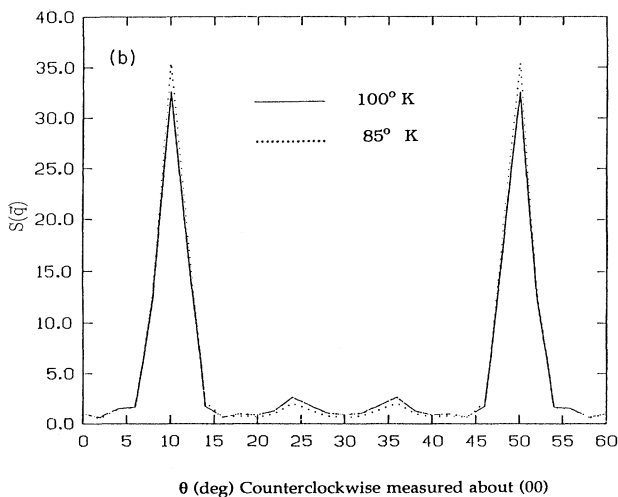
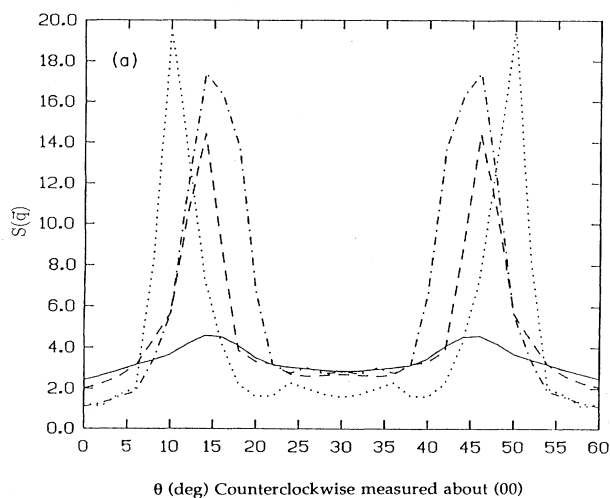


FIG. 3. (a) The angular distribution $S(q)$ at $T=300$ (solid line), 210 (dashed line), 165 (dot-dashed line), and 154 K (dotted line) within a 60° segment of the first sharp diffraction peak (FSDP) of $S(q)$ about the origin (00) for the Rb sample. Note that the rotation angle jumps across the transition temperature T_c and keeps its constancy either above or below T_c , respectively. (b) The angular distribution $S(q)$ at $T=100$ (solid line) and 85 K (dotted line) within a 60° segment of the FSDP about the origin (00), again for Rb. The rotation angle is 10° at those temperatures.

the effect of the size of the model system. We have shown here the outcomes of the largest model system, with 864 alkali-metal atoms, from which the consistent transition temperature was determined. However, for the smaller systems, especially the systems with 54, 96, 150, 216, etc. atoms, the temperature dependence curves of C_v present either a "plateau" near the transition temperature or a double peak or a bump on a main peak. This leads to difficulty in determining the transition temperature and critical properties. We suggest that this may be caused by the boundaries of the small model systems. Although periodic boundary conditions were always used in the MD simulation, the percentage of the atoms which are near the borders is too large for those small model systems to properly mimic the real system. As mentioned

above, we have found that the system with 864 atoms is the smallest model system to acquire satisfactory results for the specific heat.

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- ¹Allen M. Ferrenberg and Robert H. Swendsen, *Phys. Rev. Lett.* **61**, 2635 (1988).
²Allen M. Ferrenberg and Robert H. Swendsen, *Phys. Rev. Lett.* **63**, 1195 (1989).
³Katherine J. Strandburg, *Rev. Mod. Phys.* **60**, 161 (1988).
⁴S. C. Moss and R. Moret, in *Structural Properties and Phase Transitions, Graphite Intercalation Compounds I: Structure and Dynamics*, edited by H. Zabel and S. A. Solin, Springer Series in Materials Science Vol. 14 (Springer-Verlag, Berlin, 1990).
⁵J. D. Fan, Ph.D. thesis, University of Houston, 1989.
⁶A. Vigliante, J. D. Fan, G. Reiter, and S. C. Moss, *Phys. Rev. B* **43**, 6739 (1991).
⁷J. D. Fan, G. Reiter, and S. C. Moss, *Phys. Rev. Lett.* **64**, 188 (1990).
⁸J. D. Fan, O. A. Karim, G. Reiter, and S. C. Moss, *Phys. Rev.*

- B* **39**, 6111 (1989).
⁹S. C. Moss, G. Reiter, J. L. Robertson, C. Thompson, J. D. Fan, and K. Ohshima, *Phys. Rev. Lett.* **57**, 3191 (1986).
¹⁰X. B. Kan, J. L. Robertson, S. C. Moss, K. Ohshima, and C. J. Sparks, *Phys. Rev. B* **39**, 10 627 (1989).
¹¹P. B. Visscher and L. M. Falicov, *Phys. Rev. B* **3**, 2541 (1971).
¹²M. Plischke, *Can. J. Phys.* **59**, 802 (1981).
¹³W. G. Hoover, A. J. C. Land, and B. Morn, *Phys. Rev. Lett.* **48**, 1818 (1982).
¹⁴D. J. Evans, *J. Chem. Phys.* **78**, 3297 (1983).
¹⁵F. Rousseaux, R. Moret, G. Guerad, P. Lagrange, and M. Lalaurain, *Synth. Met.* **12**, 45 (1985).
¹⁶F. Rousseaux and R. Moret (unpublished).
¹⁷H. Seong, S. D. Mahanti, S. Sen, and T. Cagin, *Phys. Rev. B* **46**, 8748 (1992).
¹⁸G. Reiter and S. C. Moss, *Phys. Rev. B* **33**, 7209 (1986).