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Molecular-dynamics study of the temperature-dependent two-dimensional Rb liquid in graphite

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A molecular-dynamics simulation of the two-dimensional modulated liquid state of Rb intercalated in graphite is reported in which the circular average of the static structure factor, $S(q)$, is successfully fitted and the anisotropic liquid $S(\mathbf{q})$ is calculated. All of the experimentally observed modulation features are reproduced and the liquid is then cooled on the computer to yield a temperature dependent $S(\mathbf{q})$, an ordering (freezing) temperature, and an incommensurate ordered-state diffraction pattern in agreement with the data of Rousseaux and co-workers.

We present here initial results of our molecular-dynamics (MD) study of an intercalated two-dimensional (2D) Rb liquid modulated by its periodic graphite host.[1] These 2D alkali-metal liquids are attractive for MD simulation as they are uncorrelated from layer to layer and are incommensurate with their graphite hosts.[2–4] The circular average of the in-plane liquid structure factor, $S(q)$, has been experimentally determined by x-ray scattering for stage-2 Rb,[4] K,[5] and Cs,[6] in highly oriented pyrolytic graphite (HOPG) and there is considerable x-ray photographic data on the anisotropic liquid scattering from intercalated graphite single crystals.[6–9] In particular, the work of Rousseaux *et al.*[9] follows the liquid pattern in single-crystal $C_{24}Rb$ (stage 2) through the ordering temperature, providing a good test for the MD in reproducing not only the liquid and solid structures but also an estimate of the transition temperature.

In the present simulation, we fit the measured, circularly averaged, x-ray structure factor for stage-2 liquid Rb in HOPG in which each Rb layer is separated by two graphite planes. (The graphite layers bounding the Rb are positioned directly over each other.) We also calculate the full anisotropic $S(\mathbf{q})$ replicating all of the features predicted by theory[10] and observed in the x-ray single-crystal photographs.[9] Finally, we calculate $S(\mathbf{q})$ as a function of temperature. A crucial input in the simulation is the graphite-Rb modulation potential which has been derived from x-ray scattering[11,12] through a careful measurement of the (modulated) Rb contribution to the *HK.L* graphite Bragg peaks. The graphite-K potential has been evaluated in a similar fashion[12] and both Rb and K results have recently been summarized in a short review together with a preliminary MD comparison.[13]

For the MD we chose a rhombic box of 36×36 graphite unit cells, with edges parallel to the cell axes $|\mathbf{a}_1|=|\mathbf{a}_2|=2.46$ Å. Given two carbon atoms per cell, this box contains 216 Rb atoms at a planar density of $C_{12}Rb$. (With this composition, a good fit could be made to the position of the first peak in the liquid structure factor, which is often used as a measure of nearest-neighbor distance, or number density, for close-packed systems.) The repulsive part of the Rb-Rb potential was taken from the treatment of Visscher and Falicov[14] as adapted for the graphite intercalation compounds by Plischke[15] in his calculation of the 2D liquid state. The potential energy $V_p(r)$, between two ions of charge e, a distance r apart, midway between the two identical graphite planes to which the charge is donated, may be written

$$V_p(r)=\frac{e^2}{4\pi\epsilon_0}\left[\frac{1}{r}-Y(r)\right],$$

where the screening contribution $Y(r)$ is given explicitly by Plischke.[15] ϵ_0, the only unknown in this potential, may be treated as an adjustable parameter chosen to yield, with the in-plane density, a good fit to the position and shape of the first sharp peak in the liquid structure factor, $S(q)$.

The other contribution to the potential energy is the graphite modulation potential $V_m(\mathbf{r})$ induced in the Rb liquid. This takes the form[10]

$$V_m(\mathbf{r})=\sum_{H,K}V_{HK}e^{i\mathbf{q}_{HK}\cdot\mathbf{r}},$$

where $\mathbf{q}_{HK}$ is a reciprocal-lattice vector of the graphite. Values for βV_{HK} ($\beta=1/kT$) are experimentally available for Rb from the work of Thompson[16] and from a reanalysis of the data of Ohshima *et al.*,[4] both of which are supplied in Moss *et al.*[11]

The MD simulation was carried out at 300 K in the 216-atom array with periodic boundary conditions using both the AS9000 computer at the University of Houston and the Cray Research X-MP/48 computer at the National Center for Supercomputing Applications, University of Illinois at Urbana-Champaign. The time step in the simulation was a constant $\Delta t = 0.04$ ps. The total number of configurations or snapshots, N_S, over which the statistical average of the static structure factor was calculated is $N_S = 280$ with a time separation between any two adjacent shots of $100\,\Delta t$. To counter the effects of finite box size we used a convenient spline to bring $V_p(r)$ smoothly to zero at large r.

We wish to calculate both $S(\mathbf{q})$, for comparison with the scattering from intercalated single crystals,[6–9] and $S(q)$, which is its circular average appropriate to the Rb data from HOPG.[4,11,13,16] Because the $S(q)$ from HOPG has been quite accurately determined,[13,16] this was fit first. The MD result may be circularly averaged to give a correlation function $g(r)$ from which $S(q)$ is obtained as follows:

$$S(q) = 1 + 2\pi\rho_0 \int_0^\infty r[g(r)-1]J_0(qr)dr \; , \qquad (1)$$

where $J_0(qr)$ is the zeroth-order Bessel function and ρ_0 is the planar number density. With the imposed $V_m(\mathbf{r})$, however, $g(r)$ oscillates about 1.0 at large r and must be cut at the end of our periodic box. This oscillatory part of $g(r)$ can be formally written as

$$f(r) = \sum_{H,K} \langle \rho'_{q_{HK}} \rangle^2 J_0(q_{HK} r), \quad \rho'_{q_{HK}} = \frac{1}{N} \sum_i e^{i\mathbf{q}_{HK}\cdot\mathbf{r}_i} \; .$$

By replacing $[g(r)-1]$ in (1) by $[g(r)-f(r)]$, we may thus satisfy the convergence of the integral in (1) and eliminate both the ringing in the transform, $S(q)$, and the Bragg-like contribution from the modulated liquid.

Our final fit, shown in Fig. 1, was obtained by matching $S(q)$ at the first sharp peak ($q = 1.18$ Å^{-1}) to give an in-plane density of $C_{12}Rb$ and an ϵ_0 of 2.35 (compared with a free-space value of 1.0). If we assume $\epsilon_0 \equiv 1.0$, the charge transfer, e, to graphite is 0.65 electrons/Rb. We have labeled selected features in Fig. 1 for reference: a is the first sharp diffraction peak whose position scales with the in-plane density and whose width yields a correlation range, $2\pi/\Delta Q$, of ~23 Å or nearly four Rb diameters; b is a modulation shoulder on the second liquid diffuse peak at c; d is the {10.0} Bragg position of graphite, $\{HK\} = \{10\}$; and e and f compose a split third diffuse peak from the liquid.

In calculating the anisotropic structure factor $S(\mathbf{q})$, a second method was employed which did not involve the

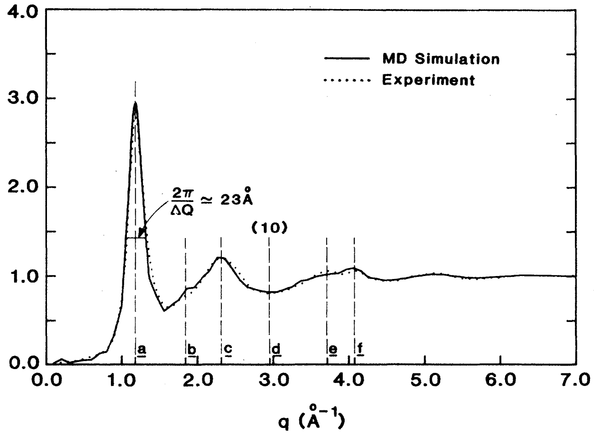

FIG. 1. Comparison of the MD simulation with the circularly averaged liquid structure factor $S(q)$ for stage-2 Rb in HOPG. A correlation range of ~23 Å is indicated, as are the prominent features in $S(q)$ at q values of a–f. The experimental graphite (10.0) peak at 2.94 Å^{-1} (d) has been removed along with the (11.0) peak at ~5.0 Å^{-1}.

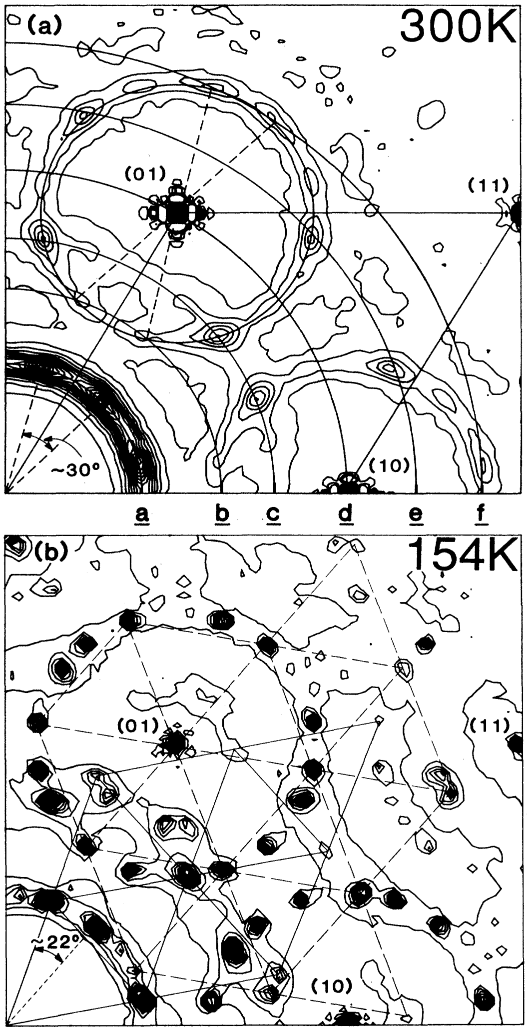

FIG. 2. Simulated structure factor $S(\mathbf{q})$ for Rb in an $HK.0$ section of a graphite single crystal. The liquid pattern in (a) shows (i) sharp Rb contributions at the {10} graphite Bragg positions; (ii) anisotropic modulated liquid scattering; (iii) development of halos about all {10} positions. The origins of a–f in Fig. 1 are indicated and the absence of a halo about (11) may be noted. The side structure on the Bragg peaks is a Fourier "ripple." The incommensurate ordered pattern in (b) is characterized by a (rotated) alkali-metal lattice (——) and its companion modulation lattice (— — —) about the graphite (01) position (all {10} points are similarly decorated).

removal of the periodic component in $g(r)$ but which otherwise gave essentially the same $S(q)$ for HOPG. In this method we treat the periodic 216-atom box used in the simulation as one supercell of an infinite lattice. Each snapshot then gives the coordinates $\mathbf{r}_i$ of the 216-atom basis set of the supercell. In this case, however, $\mathbf{q}$ is evaluated only at $\mathbf{q}_{hk} = h\mathbf{B}_1 + k\mathbf{B}_2$, where $\mathbf{A}_1 = 36\mathbf{a}_1$, $\mathbf{A}_2 = 36\mathbf{a}_2$, and $\mathbf{B}_{1,2}$ are reciprocal to $\mathbf{A}_{1,2}$. This procedure subdivides the normal graphite reciprocal lattice into (h,k) subcells at each point of which $S(\mathbf{q}_{hk})$ is evaluated; $S(\mathbf{q})$ is then given by an interpolation procedure.

Figure 2 shows $S(\mathbf{q})$ for liquid (and solid) Rb in single-crystal graphite using the supercell method with $\epsilon_0 = 2.35$ as in Fig. 1. Figure 2(a) presents the liquid scattering in a 90° segment of the graphite reciprocal lattice, obtained by first averaging the calculation over three irreducible 30° segments and then displaying the averaged result, via reflection and rotation, over the 90° segment (see Fig. 3 for a full 360° picture). There is a clear anisotropic splitting of the first sharp liquid diffraction peak at a̲ in Fig. 1 into lobes $\sim \pm 15°$ off the [10] axes, for which the ratio $I_{\max}/I_{\min} \simeq 1.7$. In the ordered incommensurate solid phase in Fig. 2(b), the alkali-metal Bragg spots that develop out of these split diffuse peaks appear rotated off the graphite [10.0] directions by ~11°, in agreement with experiment.[9] Clearly we are seeing this modulation effect in the 2D Rb liquid as observed[6-9] and predicted.[10] [While the prediction of an anisotropic $S(\mathbf{q})$ is perhaps intuitively obvious, its actual analytical description is rather complex, involving multiparticle correlations and cumbersome integrals.[10]]

Figure 2(a) also demonstrates the expected halos,[6-10] for which $S(\mathbf{q}) \Longrightarrow S(\mathbf{q}+\mathbf{q}_{HK})$, about the $\{10\}$ positions. The origins of the circularly averaged features, a̲–f̲ in Fig. 1, are also indicated. For instance, the diffuse splitting of intensity on the a circle ($q = 1.18$ Å^{-1}) is weakly reproduced in the halos about (10) or (01) as lobes, noted on the (01) halo (and on the b̲ circle and f̲ circle as the main contribution to those features in Fig. 1). The halos are not, however, symmetrical about each $\{10\}$ Bragg point because there are interferences with the normal 2D (unmodulated) liquid scattering which is pronounced around the entire c̲ circle but enhanced on the halo. As discussed below, there is a wealth of detail in $S(\mathbf{q})$ from the ordered phases[7-9,17-21] that emerges directly out of these rather faint modulation features in the liquid pattern. It should also be noted that there is no halo about the (11) reciprocal-lattice point. Theory[10] indicates that the intensity in a liquid halo will be proportional to V_{HK}^2. From Ref. 11 we may note that $\beta V_{10} = -0.45$ while $\beta V_{11} = -0.06$. We therefore expect only a very weak halo about $\{11\}$ and none about the other $\{HK\}$ positions.

Returning to the ordered state in Fig. 2(b), we have indicated both the primary incommensurate alkali-metal lattice (solid lines) and its companion modulation pattern (dashed lines) about the graphite (01) position. Every intensity feature in the MD pattern can be accounted for by this construction of a rotated alkali-metal lattice and its $\{10\}$ and (weakly) $\{11\}$ modulation satellites.

It is also gratifying to note that the primary alkali-metal (11) reflection lies directly on the modulation circle about graphite (01) as suggested by Mori *et al.*[8] and rationalized by Yamada and Naiki[18] and Suzuki and Suematsu.[19] This feature serves to confirm the domain-discommensuration model first put forth by Clarke

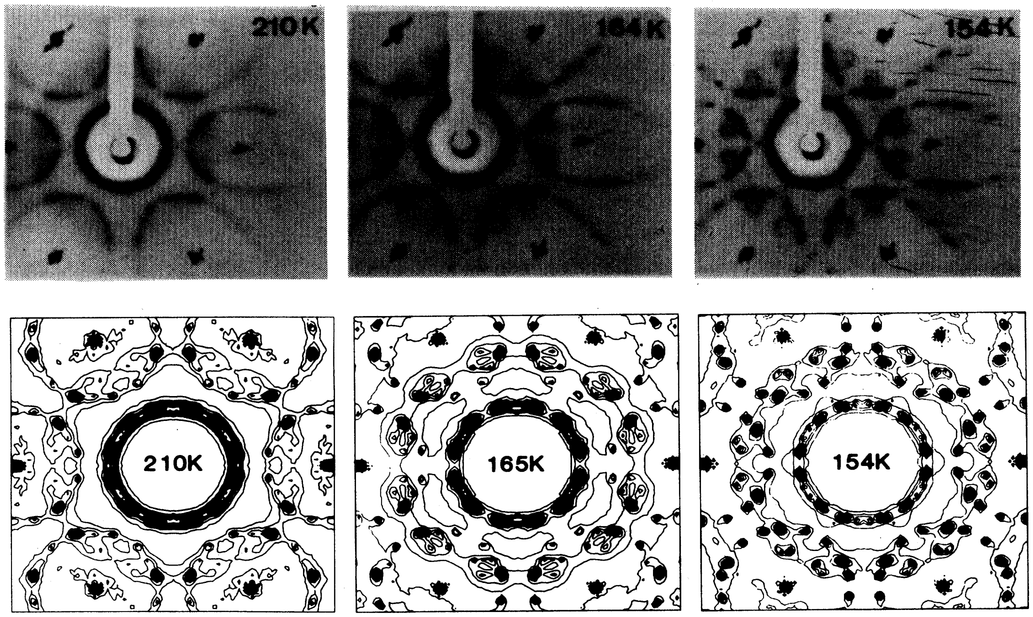

FIG. 3. Temperature dependence of $S(\mathbf{q})$ for stage-2 Rb in a graphite single crystal as studied by Rousseaux *et al.* (Ref. 9) compared to the present MD simulation. Although the cylindrical monochromatic Laue film is distorted on flattening, the detailed agreement with the MD on cooling through the ordering transition is clear.

et al.,[17] and it appears to be roughly obeyed in all of the ordered alkali-metal intercalant structures.[7–9,17–21]

A quantitative comparison of the pattern in Fig. 2(b) with accurate x-ray intensities awaits available single-crystal data. Figure 3 presents a semiquantitative comparison with the monochromatic stationary Laue photos of Rousseaux *et al.*[9] (The cylindrical films have been distorted by flattening.) The ordering transition is well captured with a calculated T_c of ~160 K, in good agreement with experiment, as determined both by a rapid change in calculated peak height and width and by a drop in rotation angle from ~15° to ~11°. The evolution on cooling of the modulation features in the liquid is well reproduced by the MD, and the agreement below T_c at 154 K, as in Fig. 2(b), is quite good, although the intensity variation around the (10) modulation circle is not identical in the two.

The overall success of the MD in reproducing both solid and liquid structures is encouraging and we are currently calculating $S(q,\omega)$ to compare with experiment.[22,23] We are also developing real-space portraits of this strongly modulated 2D liquid.

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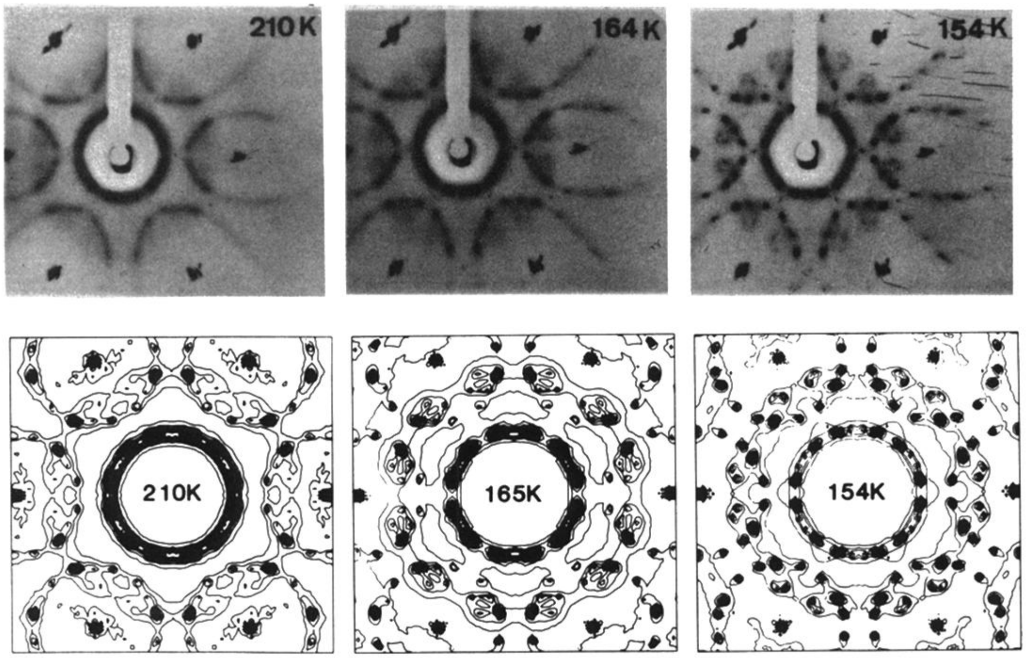

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