X-Ray Determination of the Substrate Modulation Potential for a Two-Dimensional Rb Liquid in Graphite

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(Received 6 October 1986)

Using a nonlinear-response theory that accounts for correlation in the liquid, we have determined the modulation potential for a 2D Rb liquid in graphite from a measurement of the Rb contribution to the graphite Bragg peaks. The resulting potential is almost perfectly represented by a set of six simple sine waves; its value at a hexagon center is $V_0 = -0.0735$ eV. At a bond midpoint the potential is $V_b = +0.0185$ eV. This result is checked with numerical simulations, and the implications for other 2D systems, including rare gases on graphite, are discussed.

We have recently developed[1] a detailed theory of the x-ray scattering from a two-dimensional (2D) liquid modulated by its periodic host in which the origins of the major diffraction effects are discussed. These effects include the following: (a) a δ-function-like contribution of the modulated liquid to the host Bragg peaks, (b) the replication of the liquid scattering as halos about the host reciprocal lattice points, and (c) the angular modulation of the (normally isotropic) liquid scattering. We present here the experimental determination of the modulation potential in stage-2 Rb graphite of approximate composition $C_{24}Rb$. The theory is used to extract the potential from the measured graphite Bragg intensities, and the results are checked with numerical simulations. The implications of our work for measurements of the potential between noble gases and a graphite substrate are also given.

One object of our overall program of work on these materials is to provide an accurate value of this potential for a molecular-dynamics (MD) simulation of the liquid state in the alkali-metal graphite intercalation compounds, from which the ordered state proceeds, and to determine via MD the static structure factor, $S(\mathbf{q})$, as well as a dynamic structure factor $S(\mathbf{q},\omega)$ from which

the phonon density of states[2] and diffusion[3] may be evaluated. Preliminary reports of our measurements have appeared in the Proceedings of the Tsukuba Conference[4,5] in which the techniques of both normal crystallography[4] and anomalous scattering[5] were employed on highly oriented pyrolytic graphite samples to extract values for the Rb contribution to several of the graphite peaks.

The in-plane modulation potential, $V(\mathbf{r})$, may be written

$$V(\mathbf{r}) = \sum_{H,K} V_{HK} \exp(i\mathbf{q}_{HK} \cdot \mathbf{r}), \qquad (1)$$

where $\mathbf{q}_{HK}$ is a basal-plane vector of the graphite reciprocal lattice. We wish to evaluate $\langle \rho_q \rangle$, the ensemble-averaged Fourier transform of the Rb number density which will be nonzero at the graphite reciprocal-lattice points in the presence of the periodic potential in (1). If this potential is quite small (i.e., all $\beta V_{HK} = V_{HK}/kT \le 0.1$) a linear-response theory[1,5] may be employed to evaluate $\langle \rho_q \rangle$. If, in addition, the planar liquid structure factor $S(q)$ for the Rb is unity at all the graphite HK positions, a particularly simple form for the $HK.L$ structure factor for a single layer or sandwich of C-Rb-C results[1,5]:

$$F(HK.L) = 4f_C e^{-M_C}\{\cos \tfrac{2}{3}\pi(H+2K)\cos(\pi L C_1)\} + \tfrac{1}{6}X'f_{Rb}e^{-M_{Rb}^\perp}(\delta_{q_\parallel,0} - \beta\delta_{q_\parallel,q_{HK}}V_{HK}), \qquad (2)$$

where C_1 is the ratio of the sandwich thickness to the total c axis, X' is the ratio of the ideal concentration ($\tfrac{1}{24}$) to the actual value, and $M_{Rb}^\perp$ is the Rb Debye-Waller factor along the c axis. In fact, however, the potential in the alkali graphite intercalation compounds is not so small and the liquid structure factor, $S(q)$, is appreciably different from unity at the 10.0 graphite reciprocal lattice point. In this case, more care must be taken, but an expression similar to Eq. (2) results,[1]

$$F(HK.L) = 4f_C e^{-M_C}\{\cos \tfrac{2}{3}\pi(H+2K)\cos(\pi L C_1)\} + \tfrac{1}{6}X'f_{Rb}e^{-M_{Rb}^\perp}\langle\rho'_{q_{HK}}\rangle. \qquad (3)$$

$\langle \rho'_{q_{HK}} \rangle$ is simply the normalized value of $\langle \rho_q \rangle$ evaluated at the Bragg peaks

$$\langle \rho'_{q_{HK}} \rangle = N^{-1} \langle \sum_i \exp(i\mathbf{q}_{HK} \cdot \mathbf{r}_i) \rangle, \tag{4}$$

where the $\mathbf{r}_i$ are the in-plane positions of Rb atoms. $\langle \rho'_{q_{HK}} \rangle$ is given by[1]

$$\langle \rho'_{q_{HK}} \rangle = [F_1(\mathbf{q}_{HK})/F_1(0)]\exp[F_2(\mathbf{q}_{HK}) - F_2(0)], \tag{5}$$

where

$$F_1(\mathbf{q}_{HK}) = \int_0^a \int_0^a \exp(i\mathbf{q}_{HK} \cdot \mathbf{r})\exp\left[-\beta \sum_{H',K'} V_{H'K'} \exp(i\mathbf{q}_{H'K'} \cdot \mathbf{r}) \right] d^2r \tag{6}$$

and

$$F_2(\mathbf{q}_{HK}) = \sum_{H',K'} F_1(\mathbf{q}_{H'K'})F_1(-\mathbf{q}_{HK} + \mathbf{q}_{H'K'})[S(\mathbf{q}_{H'K'} - 1)]/F_1(0)F_1(\mathbf{q}_{HK}). \tag{7}$$

If the value of $S(\mathbf{q}) = S(\mathbf{q}_{HK})$ is unity at all values of $\{HK\}$, $F_2(\mathbf{q}_{HK}) = F_2(0) = 0$, and we need only the integrals for $F_1(\mathbf{q})$. The effect of correlation in the liquid on the estimate of the δ-like Bragg part arises because the response of the liquid is not that of a random dense gas. The $S(q_{HK})$ that enters Eq. (7) is actually that of the unperturbed (isotropic) liquid, which is not experimentally accessible. Numerical calculations[6] show, however, that at the values of βV_{HK} of interest, it is not far from the circular average of the actual $S(\mathbf{q})$. Figure 1 addresses this issue. Figure 1(a) presents an experimental $S(q)$ from stage-2 Rb in highly oriented pyrolytic graphite derived from the data taken at the Stanford Synchrotron Radiation Laboratory,[7] in which the sharp Bragg peaks at $q = 2.94$ Å^{-1} (the 10.0 trace of 10.1) and at $q = 5.09$ Å^{-1} (11.0) have been easily removed. In addition the data have been somewhat smoothed to remove small subsidiary bumps associated with the circular average of the modulation halos noted earlier.[4] This circularly averaged and smoothed $S(q)$ is used in Eq. (7) for the correction.

Figures 1(b) and 1(c) show the influence of the liquid correction on the estimate of $\langle \rho'_{q_{HK}} \rangle$. In Fig. 1(b) $\beta V_{10} = -0.10$, which is appropriate for the linear response theory, and we thus may calculate the values of $\langle \rho'_{q_{HK}} \rangle$ for $HK = 10$, 11, and 20 as a function of Rb in-plane density by letting the 10.0 graphite position, referred to as Q_{10}, vary as the abscissa. [$S(q)$ from Fig. 1(a) is thus entered in Eq. (7) but the graphite spacing is varied.] When $Q_{10} = 2.94$ Å^{-1}, the actual experimental situation, represented by Fig. 1(a), prevails. As Q_{10} decreases, it is the same as decreasing the alkali-alkali spacing. When Q_{10} comes at the peak, $S_p(q)$, in the alkali structure factor, namely $S_p(q) \cong 1.19$ Å^{-1}, the alkali may easily register and certain pathologies are introduced into $\langle \rho'_{q_{10}} \rangle$, $\langle \rho'_{q_{11}} \rangle$, and $\langle \rho'_{q_{20}} \rangle$. Otherwise, for $\beta V_{10} \cong -0.10$, only $\langle \rho'_{q_{10}} \rangle$ survives and its value smoothly and weakly oscillates about $\langle \rho'_{q_{10}} \rangle \cong 0.10$; i.e., $\langle \rho'_{q_{10}} \rangle \cong \beta V_{10}$ as in Eq. (2).

When $\beta V_{10} \cong -0.50$, which is close to its experimental value, $\langle \rho'_{q_{HK}} \rangle$ is appreciable for all values of Q_{10} with $\langle \rho'_{q_{11}} \rangle$ and $\langle \rho'_{q_{20}} \rangle$ becoming truly pathological as Q_{10} pass

over the $S_p(q) = 1.19$ Å^{-1}. [All three also peak slightly when Q_{11} and Q_{20} pass over $S_p(q)$.] The anomalous behavior may be understood from an examination of the structure of the equations (5)–(7); suffice it here to note that, again, away from $Q_{10} \cong 1.19$ Å^{-1}, $\langle \rho'_{q_{HK}} \rangle$ behaves smoothly and predictably. This is important in the application of these techniques to the assessment of the substrate potential for other 2D fluids, with smaller atom sizes, for which the existence of a hexatic phase[8] has been discussed.[9] For example, monolayer xenon, krypton, and argon on graphite have an $S_p(q) \cong 1.50$, 1.70, and 2.00 Å^{-1}, respectively,[10] but a potential which should be considerably weaker than for alkali graphite. Figure 1(b) suggests that for the liquid state of all of these rare-gas monolayers on graphite, a substrate potential can be evaluated from an estimate of the monolayer contribution to the graphite peaks. In fact, when the potential is weak, as in Fig. 1(b), only the 10 graphite reciprocal lattice rod needs to be measured (with and without the gas layer) to extract a good estimate of this potential!

We turn now to the determination of βV_{HK} from the experimental $\langle \rho'_{q_{HK}} \rangle$. There are two sets of data from which we may obtain $\langle \rho'_{q_{HK}} \rangle$. The first is the data of Ohshima, Moss, and Clarke[4] in which 85 Bragg peaks were measured and their integrated intensities estimated. Because several sets of these $(HK.L, H - K \neq 3$ m) were broadened by stacking faults, this estimate was often difficult. The entire data set has nonetheless been reanalyzed to determine $\langle \rho'_{q_{HK}} \rangle$ from L scans at fixed HK. The results of an iterative least-squares fit are given in Table I. Included also in Table I, except for $HK = 20$, is a set of $\langle \rho'_{q_{HK}} \rangle$ determined from anomalous scattering experiments at the Stanford Synchrotron Radiation Laboratory both by profile analysis of the faulted peaks and by a new energy ratio method.[7] Both methods will be reported elsewhere.[7] The agreement between the two sets of $\langle \rho'_{q_{HK}} \rangle$ on different samples, with slightly different in-plane densities, (X'), is very gratifying.

The procedure for evaluating βV_{HK} with use of Eqs. (5)–(7) introduces the experimental values of $\langle \rho'_{q_{HK}} \rangle$
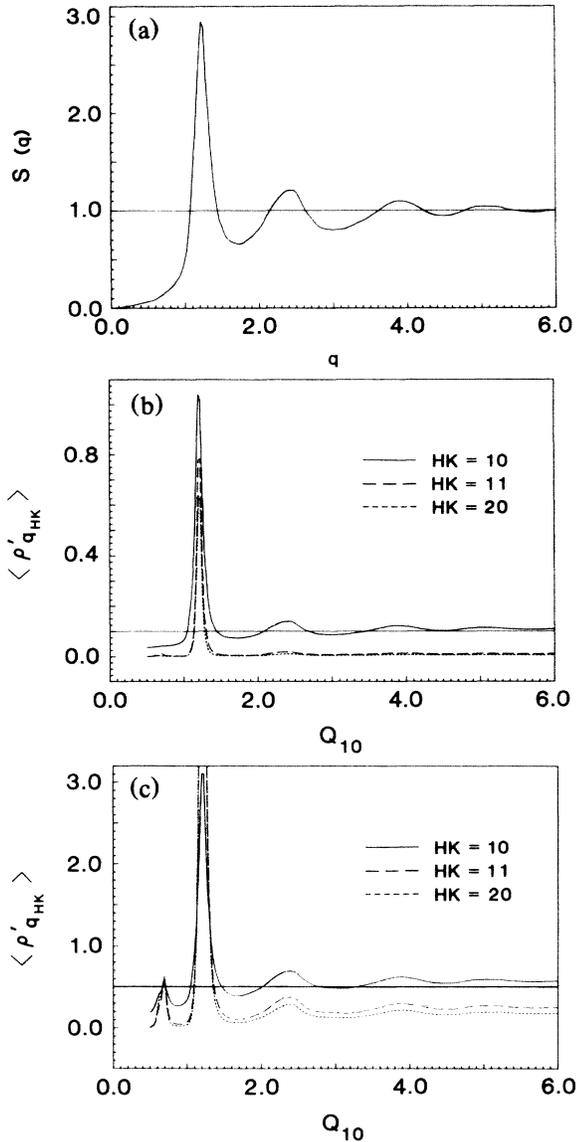
FIG. 1. (a) The smoothed experimental 2D Rb liquid structure factor $S(q)$ for $C_{24}Rb$, with the (10.0) and (11.0) Bragg contributions, at $q = 2.94$ and 5.09 Å^{-1}, removed. (b) and (c) $\langle \rho'_{q_{HK}} \rangle$ ($HK = 10,11,20$) are evaluated with use of Eqs. (5)–(7), with only βV_{10} and the data in (a) as input, plotted vs an effective graphite reciprocal spacing, Q_{10}. When $Q_{10} = 2.94$ Å^{-1}, the experimental situation prevails. As Q_{10} decreases, we explore the effect on $\langle \rho'_{q_{HK}} \rangle$ of a decreased alkali-alkali spacing. Except for the region where $Q_{10} \cong S_p(q)$, the peak position in (a), $\langle \rho'_{q_{HK}} \rangle$ varies smoothly with Q_{10}. For $\beta V_{10} = -0.10$, (b) shows that $\langle \rho'_{q_{10}} \rangle \cong -\beta V_{10}$ and that $\langle \rho'_{q_{HK}} \rangle = 0$, $\{HK\} \neq \{10\}$. For $\beta V_{10} = -0.50$, part (c) indicates an appreciable contribution to $\{HK\} \neq \{10\}$ as measured.

TABLE I. The measured rubidium contribution to the graphite structure factor together with the average of the values of βV_{HK} calculated via Eqs. (5)–(7). The last column uses βV_{10} in an MD simulation to compare with the input data.

HK	$\langle \rho'_{q_{HK}} \rangle$ Ref. 2	Ref. 7	βV_{HK}	$\langle \rho'_{q_{HK}} \rangle$MD Ref. 6
10	0.48 ± 0.03	0.48 ± 0.03	-0.45	0.48
11	0.19 ± 0.03	0.22 ± 0.03	-0.06	0.18
20	0.14 ± 0.02	...	-0.01	0.13
21	0.04 ± 0.02	0.04 ± 0.02	0.03	0.04
30	0.05 ± 0.02	0.03 ± 0.02	-0.01	0.02
22	0.02 ± 0.02	0.00 ± 0.04	-0.02	~ 0

the use of Newton's method. Then nonlinear regression analysis is used to refine the true position of the equilibrium minimum. The speed of convergence and agreement between input and output $\langle \rho'_{q_{HK}} \rangle$ indicate a successful set of βV_{HK}'s, given in Table I as the average for the two data sets.

What is remarkable and physically satisfying is that for both sets essentially only βV_{10} survives, i.e., that the modulation potential is basically a set of six simple sine waves along the [10.0] directions. We also include in Table I the set of $\langle \rho'_{q_{HK}} \rangle$'s obtained from our initial MD simulations[6] on a 736-atom system in which a simple repulsive Yukawa potential, chosen to give agreement with $S(q)$, was used for the interacting Rb ions, confined to the periodic box, together with the experimental substrate modulation potential evaluated by use of only βV_{10} from Table I with Eq. (1). It is straightforward to extract $\langle \rho'_{q_{HK}} \rangle$ from the average of many MD snapshots. The agreement with the input data is important because it indicates that the three particle and higher order correlations not considered in Eqs. (5)–(7) are not significant for these Bragg peak contributions and that

from Table I and a trial set of $\beta V_{H'K'}$ along with the experimental $S(q_{H'K'})$ from Fig. 1(a) on the right-hand side. First, the sum of the squared differences between the experimental and calculated $\langle \rho'_{q_{HK}} \rangle$ is minimized with
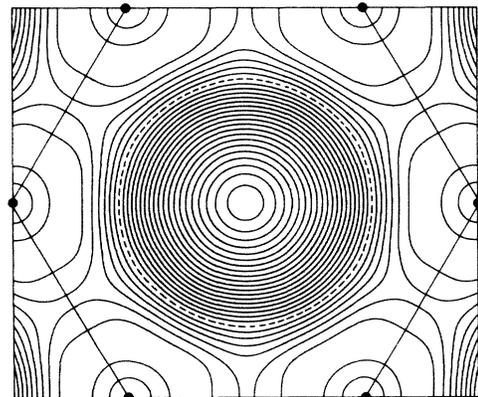
FIG. 2. The substrate modulation potential, $V(r)$, for a stage-2 Rb liquid in graphite. The contours are in steps of 0.0037 eV and the change from attractive [$V(r) < 0$] to repulsive is noted as a dashed contour. $V(r = 0) = -0.0735$ eV.

βV_{10} suffices.

Finally, in Fig. 2 we present, from Eq. (1) and Table I, the experimentally derived $V(\mathbf{r})$ for $C_{24}Rb$ within a graphite hexagon which is attractive at the center ($V_0 = -0.0735$ eV) and repulsive at the carbon atoms. At the saddle point, between two carbons along a bond, the potential $V_b = +0.0185$ eV. The difference between these two is $\Delta V = 0.092$ eV which may be compared to the barrier height, E_1, of between 0.05 and 0.10 eV for the Rb diffusion in $C_{24}Rb$.[3,11]

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