Dynamics of a 2D Liquid on a Periodic Substrate: Rb in Graphite

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We present a molecular-dynamics simulation of the dynamical properties of a 2D Rb liquid intercalated in a periodic graphite host. Using an 864-atom system we show that this dynamical response consists of both solid and liquid features well above the melting point, as indicated in the neutron experiments of Zabel and co-workers, and may be characterized by floating (time-dependent) domains of briefly registered ions which, during their ~26-ps lifetime, show phononlike behavior and a Debye-Waller factor in excellent agreement with the experiments of Kamitakahara and Zabel.

We present here calculations of the dynamical structure factor, $S(q,\omega)$, of a two-dimensional (2D) liquid of Rb intercalated in graphite, including an estimate of the diffusion constant and the vibrational properties. We also offer a time-dependent real-space picture of the Rb-atom distribution in its periodic graphite host at room temperature. The molecular-dynamics (MD) method has previously been used by us to simulate the static alkali-metal structure and its temperature dependence.[1,2] The input potential in this simulation consisted of a screened Coulombic repulsive interaction together with an experimentally determined graphite-host modulation potential.[2,3] The agreement with both the room-temperature $S(q)$ from highly oriented pyrolytic graphite (HOPG)[1,2] and the temperature-dependent single-crystal data of Rousseaux et al.[2,4] was quite good, including the estimate of a freezing temperature of about 160 K. The system is additionally ripe for dynamical comparison due to extensive studies of the (intercalated) alkali-metal photon density of states using incoherent inelastic neutron scattering[5] and of the planar alkali-metal diffusion using quasielastic neutron scattering.[6] In particular, Zabel and co-workers[6] have identified two physical components in their quasielastic broadening of $S(q,\omega)$ from 2D liquid Rb: (1) a fast diffusing liquid-like component and (2) a long-lived "solid" part whose width falls within the instrumental resolution and whose vibrational properties are presumably responsible for the photonlike peaks in $S(q,\omega)$. Both of these components appear directly in our calculations,[7] which represent, to our knowledge, the first successful comparison of the MD method with the dynamical response of a 2D liquid on a periodic substrate and, as such, should be applicable to other related systems.

The MD calculations were performed on a 2D periodic array of 864 Rb atoms in a rhombohedral box of 72×72 graphite unit cells with an overall planar composition of $C_{12}Rb$. The extended size of this system, which is otherwise identical to the smaller one studied in Refs. 1 and 2 (216 atoms), was important for assessing longer-time behavior. The integration time step in the MD was 0.02 ps

and the system was sampled at $5\Delta t = 0.1$ ps and run for 50 ps. The averages were taken over 100 initial times in order to replicate the appropriate statistical-mechanical average given below in Eq. (1). All other details of input potential and calculational procedures are contained in Refs. 1, 2, and 8.

We initially calculate the time correlation function of the alkali-metal density, often referred to as the intermediate scattering function $F(q,t)$, where

$$F(q,t) = N^{-1} \sum_{mn} \langle e^{-i\mathbf{q} \cdot [\mathbf{r}_m(t) - \mathbf{r}_n(0)]} \rangle, \tag{1}$$

and the notation $\langle \rangle$ specifies an average over initial conditions of the particles and over angles in q space; $\mathbf{r}_m(t)$ is the position of the mth particle at t. The angular average gives us a scalar function for the in-plane scattering in HOPG. $F(q,t)$ in the 2D case is thus given by

$$F(q,t) = N^{-1} \sum_{mn} \langle J_0(q \, | \, \mathbf{r}_m(t) - \mathbf{r}_n(0) \, | \,) \rangle, \tag{2}$$

where J_0 is the zero-order Bessel function. The function of $F(q,t)$ can be separated into two parts expressed by

$$F(q,t) = F_S(q,t) + F_D(q,t)$$

and referred to as the "self" (S) and "distinct" (D) parts. They are represented, respectively, by terms in Eq. (2) for which $m = n$ and $m \neq n$.

For present purposes it suffices to discuss $F_S(q,t)$ which, for two values of q, is shown in Fig. 1 and consists of two separated parts denoted by

$$F_S(q,t) = F_\delta(q,t) + F_{d+ph}(q,t)$$

indicating the long-lived "solid" (δ) and short-lived diffusional plus vibrational (d+ph) parts, respectively. This separation was motivated by the work of Zabel and co-workers.[6]

There are three distinct features in Fig. 1: (1) the long-lived component indicated by a dotted line; (b) the q dependence of its damping rate; (c) the damped oscillatory component. It is this latter contribution to $F_S(q,t)$ that contains both the diffusional behavior and
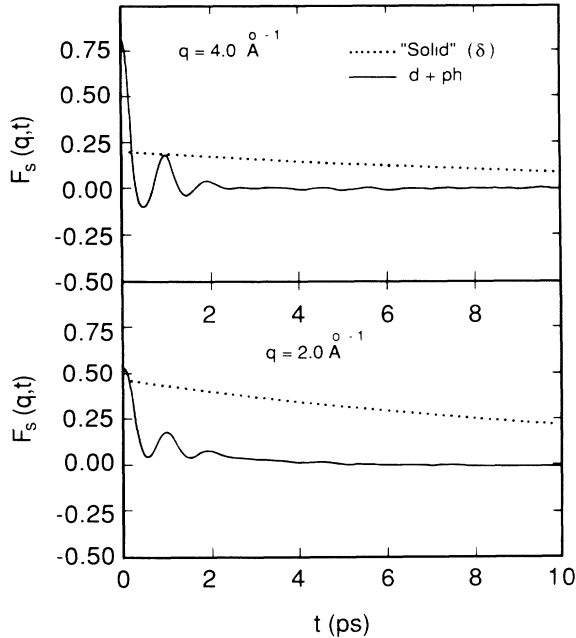
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FIG. 1. The self part of the intermediate scattering function, $F_S(q,t)$ at $q=2.0$ and 4.0 Å^{-1}. This contribution is separated into δ ("solid") and d+ph components by fitting the solid component by $b\exp(-\delta t)$ at large t where d+ph$\rightarrow 0$. A Debye-Waller factor may be retrieved from the dependence of b on q as in Eq. (5).

the phononlike excitations in $S(q,\omega)$ at appreciable q and ω in Fig. 2, as discussed below.

The dynamical structure factor $S(q,\omega)$ is determined by

$$S(q,\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty}F(q,t)e^{i\omega t}dt .$$

In the incoherent limit at high q, $S(q)\rightarrow 1.0$ and $F(q,t)\rightarrow F_S(q,t)$. We may also show that

$$\int_{-\infty}^{\infty}S_S(q,\omega)d\omega = F_S(q,0) = S_S(q) \equiv 1.0 ; \qquad (3)$$

i.e., the self part of the *static* structure factor is the constant 1.0 about which the coherent (distinct) scattering oscillates. Correspondingly, we may write the separated dynamical structure factors

$$S_S(q,\omega) = S_\delta(q,\omega) + S_{d+ph}(q,\omega) ,$$

where δ denotes the narrow solidlike peak in the spectral function at $\omega=0$ and d+ph are the diffusion (d) plus phonon (ph) parts which are more extended along the ω axis.

Figure 2 shows the Fourier transform of the separate parts in Fig. 1 at $q=4.0$ Å^{-1}. The solid part is similar to that measured by Zabel and co-workers[6] although it is considerably narrower than the instrumental resolution in their neutron experiment. The diffusion and phonon parts are clearly identifiable although they are grouped
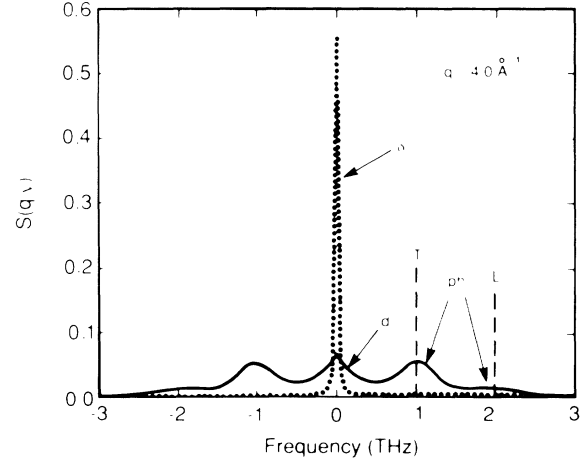

FIG. 2. The time Fourier transform of $F_S(q,t)$ in Fig. 1 at $q=4.0$ Å^{-1}. The separate components are labeled including an assignment of longitudinal ("L") and transverse ("T") branches to the vibrational spectrum. The diffusional part loses its (predicted) Lorentzian shape as the wave vector q increases.

together in $F_{d+ph}(q,t)$. The experimental observations[5] of (presumed) transverse phonons at ~ 1 THz with a small peak due, again presumably, to longitudinal phonons at ~ 2 THz are reproduced here along with the broad diffusional component centered on $\omega=0$ ($v=0$).

We may write for the δ-like part of $F_S(q,t)$,

$$F_\delta(q,t) = be^{-\delta t} , \qquad (4)$$

where according to Eq. (3), taking into account the Debye-Waller effect,

$$b = b_0\exp[-\langle\Delta x^2\rangle q^2] . \qquad (5)$$

$\langle\Delta x^2\rangle$ is the mean-square amplitude of displacement of an atom about its equilibrium position in the solidlike component. This way of describing the vibrating solid component emphasizes its crystal-like aspect with a q^2-dependent Debye-Waller damping. A companion aspect of the solid part is its own diffusional behavior; i.e., it is not a solid but only a long-lived solidlike fluctuation which slowly diffuses away. The Fourier transform of Eq. (4) in Fig. 2 is

$$S_\delta(q,\omega) = \frac{b}{\pi}\frac{\delta}{\omega^2+\delta^2} , \qquad (6)$$

which is the appropriate form for the unresolved Lorentzian component measured by Zabel and co-workers[6] as a δ-function response. While the diffusion component is associated with the liquid behavior, the phonon part is also associated with the solid. In fact, as the δ-function contribution is damped with increasing q the intensity is fed into the phonon contribution. But this latter part, oscillating in t, is also damping out rather fast in q.
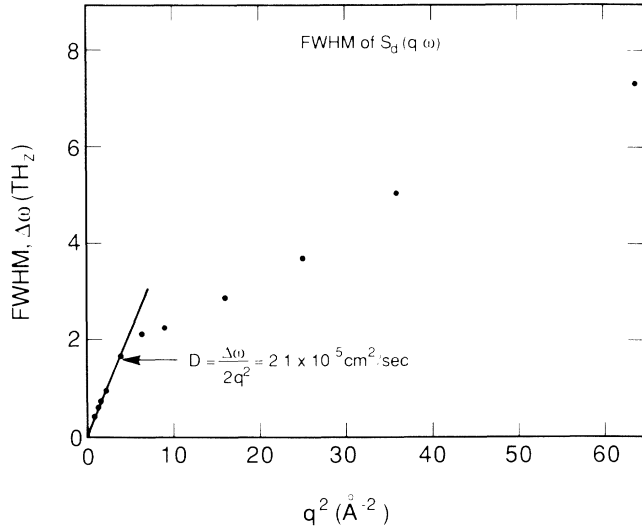
FIG. 3. The width of the liquidlike diffusional contribution, $S_d(q,\omega)$, centered on $\omega=0$ ($v=0$) in Fig. 2, vs q^2. At low q, in the hydrodynamic limit, $\Delta\omega=2Dq^2$; at $q=4.0$ Å^{-1}, as in Fig. 2, this relationship is no longer obeyed.

FIG. 4. The number of atoms, as represented by crosses in the inset, whose averaged positions remain within 0.22 Å of their initial hexagon centers as a function of time. As t increases finally all atoms exit from their original hexagons and this number approaches zero exponentially with a lifetime, δ^{-1}, of ~26 ps (solid curve). Inset: The positions of those Rb atoms still remaining after 3 ps; it may be thought of as a snapshot of a floating-domain pattern.

From Eq. (5), a plot of $\ln b$ vs q^2 was made, the slope of which, via a least-squares fit, yields a value of $(\langle \Delta x^2 \rangle)^{1/2}=0.23$ Å (Ref. 7) compared to the experimental value of 0.22 Å.[5]

As the diffusion part is associated with the fast diffusion, it can also be described by $\exp(-\alpha t)$, where α is considerably larger than δ in Eqs. (4) and (6), and, for small q, i.e., under the hydrodynamic limit,[8] is given as $\alpha=Dq^2$ with D the diffusion constant. This is shown in Fig. 3 as the FWHM in $\Delta\omega=2Dq^2$, where, for $q \leq 2.0$ Å^{-1}, D is found to be 2.1×10^{-5} cm²/s compared to the experimental value of ~2.0×10^{-5} cm²/s.[9] As q increases beyond the hydrodynamic limit, α has a more complicated relation to q and the shape of $S_d(q,\omega)$, as in Fig. 2 at $q=4.0$ Å^{-1}, is no longer Lorentzian.

We now turn to real space for insight into this dynamical process. It is possible to classify the atoms into two categories with Zabel and co-workers:[6] One is undergoing liquidlike diffusional motion represented by $F_d(q,t)$, while atoms in the other, described by $F_\delta(q,t)$, are vibrating about hexagon centers, as given by $F_{ph}(q,t)$, and are then hopping from one hexagon to the next. In this description, of course, the atoms are exchanging their categories continuously. The motion represented by $F_d(q,t)$, can be thought of as a true liquidlike diffusion somewhat impeded by the substrate. In fact our recent simulations of the unmodulated liquid reveal none of the complex substrate-induced behavior reported in this paper; they yield only conventional liquid diffusion with $D=4.7\times10^{-5}$ cm²/s.[10] The experimental linewidth in $S_D(q,\omega)$, the *coherent* scattering from the modulated liquid,[6] shows a familiar q dependence including de Genne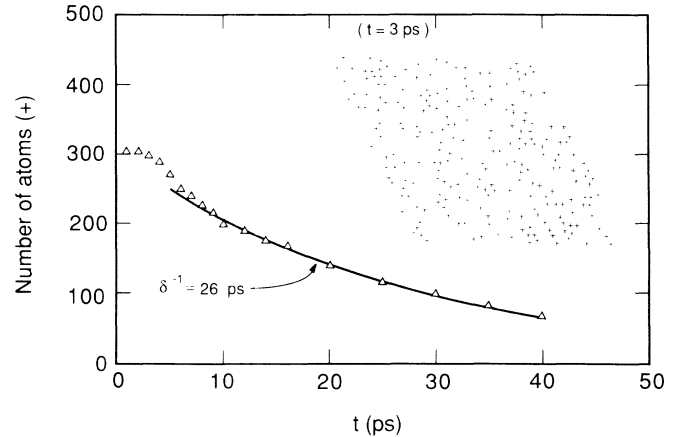s narrowing at the peak of the static liquid structure factor, $S(q)$. In other words, the modulated liquid behaves in many respects like a conventional liquid with a smaller diffusion constant.

If we focus our attention on the solidlike part of the atomic behavior, we can expect that the total number of atoms within a disk of thermal radius, $r_{th}=(\langle \Delta x^2 \rangle)^{1/2}=0.22$ Å at 300 K, remains constant for a period while undergoing vibration and then decreases exponentially because of hopping. We have therefore averaged the atom positions for each particle over a few choices of time origin for a variety of time periods from 1 to 40 ps. If the averaged position remains within the disk of 0.22-Å radius, the atom is denoted by a cross as shown in the inset of Fig. 4 for $t=3$ ps, whereas, if it leaves its disk, the atom disappears from our figure. The triangles in Fig. 4 represent the total number of atoms (crosses) remaining within their initial thermal disks for different time periods; this number stays constant until ~3 ps and then gradually damps, as least-squares fitted by the solid exponential curve, with a time constant of ~26 ps. The time constant (lifetime) of ~26 is in good agreement with the 25 ps obtained from δ in Eqs. (4) and (6) for $q=1.0$ Å^{-1}. (The solid- or δ-like component dominates only for small q.)

The constant number of crosses at small t in Fig. 4 takes on a value of ~300 atoms out of the total number of atoms, 864, in the system under consideration. This fraction of ~0.35 may be compared to the experimental estimate of 0.36 from Zabel and co-workers[6] for the fraction of the solidlike component at 300 K. The constancy over 3 ps apparently indicates that the solidlike behavior of our 2D Rb liquid at room temperature remains for several vibrational periods and implies a

coexistence of liquid and solid "phases" where the solid component gradually decays by the loss of atoms (which, of course, joins new domains). In other words, the solid-like part is associated with rather long-lived domains in which the atoms are temporarily registered and vibrating about hexagon centers; over time, they acrete or lose atoms and thus "float" about.

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