Critical Fluctuations in the Paraelectric Phase of $NaNO_2$

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Molecular-dynamics calculations have been used to investigate the nature of critical fluctuations in the paraelectric phase of $NaNO_2$. Although the $(NO_2)^-$ anions are found to reorient rapidly, predominantly about the crystal c axis, the simulation reveals the existence of long-lived fluctuations of antiferroelectric character. The reorientational motion is found to couple to optic rather than acoustic modes, in agreement with a recent theoretical prediction.

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We present the main results of a molecular-dynamics (MD) simulation of the paraelectric phase of $NaNO_2$ which was carried out in order to cast light on the nature of the various collective modes that exist in this orientationally disordered crystal.[1] At the same time we have examined the reorientation mechanism of the $(NO_2)^-$ anions and also studied the coupling of this reorientation to the translational motions.[2] Our principal finding is that even though the individual anions reorient rather frequently, long-lived (quasistatic) antiferroelectric correlations persist in the paraelectric phase. We suggest that it is these correlations that are responsible for the critical scattering observed in neutron experiments.[3,4]

Under normal pressure $NaNO_2$ has an orthorhombic structure and, for an ionic material, a low melting point (281 °C). The room-temperature phase is ferroelectric with the dipole moments of the anions aligned along the crystallographic b direction. When heated above about 164 °C it becomes paraelectric, the dipoles being disordered with respect to the b axis. The transition from a ferroelectric to a paraelectric phase goes via an intermediate phase (that exists for only 1.5 °C) in which the dipole moments of the anions are sinusoidally modulated along the a direction, with an incommensurate wave vector.[1,5] The phase transitions are not accompanied by any anomaly in the acoustic branches of the phonon spectrum.[3,4]

In the high-temperature paraelectric phase, which is our concern here, quasielastic scattering from critical fluctuations was found to persist to temperatures well above the transition from the intermediate phase.[3,4] Moreover, the energy distribution of neutrons scattered from these fluctuations implied that they were long lived, the estimated relaxation time at 200 °C being of the order of 50 ps and at lower temperatures considerably longer than this.[3]

Recent theoretical work on $NaNO_2$ has focused on the theory of the incommensurate structure[5] and the coupled dynamics of translations and rotations in the paraelectric phase.[2] No discussion or acceptible explanation has yet been offered for the origin of the critical scattering.[3,4]

Our MD calculation employed an orthorhombic cell ($4a \times 4b \times 4c$), periodic boundary conditions being used to simulate the infinite crystal. Rigid $(NO_2)^-$ ions were initially confined to the bc crystal planes with dipole moments randomly oriented along the b direction. If we label the (a,b,c) directions (x,y,z), our system consisted of eight yz sheets each containing sixteen anions. The state condition employed in the MD calculation ($T \sim 218$ °C) and the system size were dictated in part by the observation[4] that the wavelength of the critical fluctuations is about $4a$ at 204 °C. The short-range interactions between the ions were represented by Born-Meyer potentials constructed from parameters in the literature and the charge distribution of $(NO_2)^-$ was modeled by fractional charges placed on N and O atoms[6] such that the total charge was $-|e|$. The calculation of the energies and forces was handled by an Ewald method and a time step of 3×10^{-15} s was used to integrate the equations of motion. Our use of classical mechanics is justified because even the optic modes are thermally excited in the paraelectric phase. After a suitable period of equilibration, the data from 2000 time steps was saved for later exploitation. The length of our calculation implies that phenomena that occur with relaxation times greater than about 3 ps will appear to be quasistatic.

We first consider recent theoretical predictions concerning the motion of the nitrite ions.[2] By examination of individual ions over the course of the simulation we have established that $(NO_2)^-$ ions reorient predominantly about the c axis, the mean reorientation time being about 1.2 ps. However, this is *not* an exclusive mechanism; occasional flips about the a axis have also been observed.

We have examined the collective (phonon) modes via the usual time correlation function appropriate to neutron scattering, $F(\vec{Q},t)$ where $\vec{Q}$ is the momentum transfer.[7] Figure 1 shows typical examples of longitudinal acoustic (LA) and transverse acoustic (TA) phonons that are propagating in our system. The frequencies deduced from the periodic oscillations are in good agreement with the available neutron data[3,4] and hence give support to the validity of our model. There is no evidence of these longer-wavelength phonons being shifted to anomalously low frequencies by the effect of translation-rotation coupling, as seen for example in cyanide crystals.[8] The long-wavelength TA mode propagating along the a axis (not shown in Fig. 1) also behaves normally as found in a recent experiment.[3] On the other hand, the longitudinal optic (LO) and transverse optic (TO) modes obtained by autocorrelation of the positions of the centers of mass (see Fig. 2) reveal high-frequency oscillations superimposed on a slower periodic variation that is comparable to the mean reorientation time. Hence it is the optic modes that couple to the reorientation of the $(NO_2)^-$ anions. This finding confirms a recent theoretical prediction.[2]

We now turn to a discussion of fluctuations in the crystal polarization. Anticipating our results we focus only on the spatial variations in the a direction. Let the component of the dipole moment of anion j along the b axis be $\mu_y^{(j)}(\bar{x},t)$, where $\bar{x}$ is the mean position of the yz sheet that contains j. The normalized dipole moment of this sheet at time t is then $m_y(\bar{x},t)=\sum_j\mu_y^{(j)}(\bar{x},t)/16$, and the mean dipole moment of the whole crystal is $M_y=\sum_i\langle m_y(\bar{x}_i)\rangle/8$, where the brackets indicate an average over the MD run. The fact that within our statistical uncertainty we find $M_y=0$ (as well as the analogous quantities M_x and M_z)

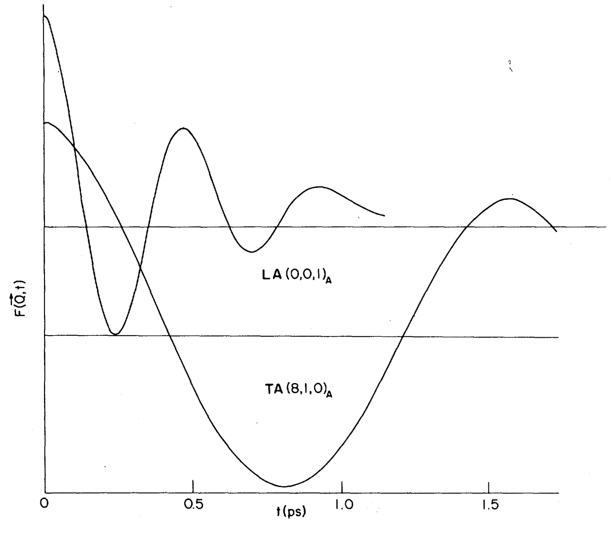

FIG. 1. The intermediate scattering function $F(\vec{Q},t)$ for selected LA and TA phonons propagating in the paraelectric phase of $NaNO_2$. The components of $\vec{Q}$ are given in parentheses in units of $2\pi/4a$, $2\pi/4b$, and $2\pi/4c$, respectively, and the subscript A indicates that in the evaluation of $F(\vec{Q},t)$ each atom was weighted by its coherent scattering length (Ref. 7).

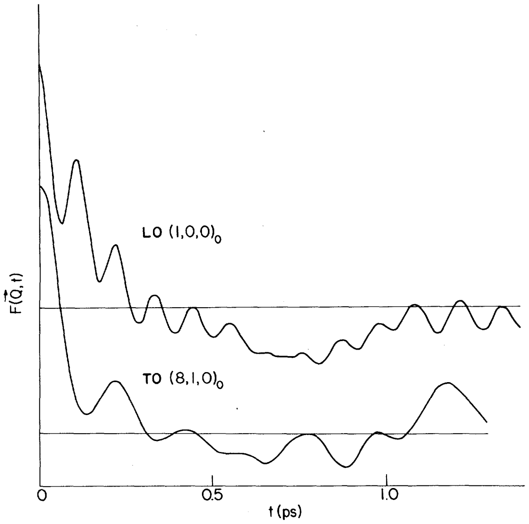

FIG. 2. As for Fig. 1 but for optic phonons. The subscript 0 indicates that in evaluating $F(\vec{Q},t)$ only the motion of the centers of mass was considered, the scattering length for the cations (anions) being given the value +1 (−1).

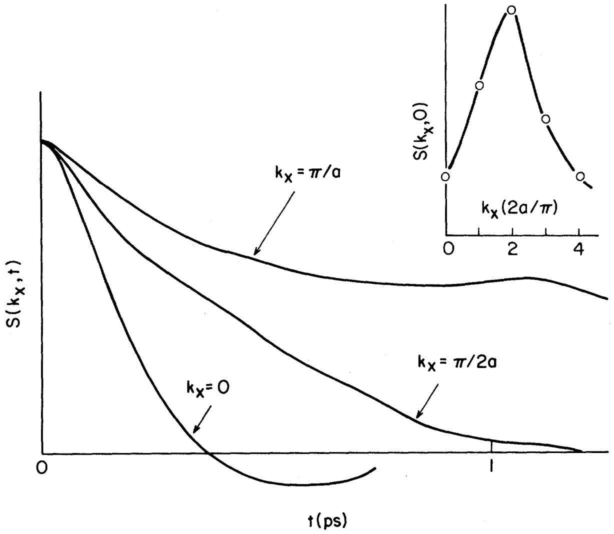

FIG. 3. Autocorrelation function of the sheet dipoles, $S(k_x, t)$. The curves have been normalized to the same value at $t = 0$. Only when $k_x = \pi/a$ is the behavior quasistatic (see text). Inset: The variation of $S(k_x, 0)$ with k_x.

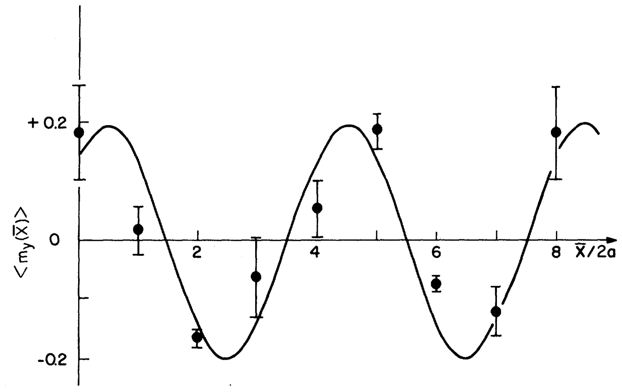

FIG. 4. Variation of the sheet dipole moment $\langle m_y(\bar{x})\rangle$ in the a direction (see text). The solid line, which has a wavelength of $2a$, is drawn as a guide to the eye. The error bars indicate the effect of averaging over half the MD data.

confirms that we have simulated a paraelectric crystal.

The dynamic critical fluctuations are described by a time correlation function, for the dipole moments of the yz sheets, of the form

$$S(k_x,t) = \langle m_y(k_x,t) m_y(-k_x,0)\rangle,$$

where k_x is the appropriate wave vector in the a direction and

$$m_y(k_x,t) = \sum_i m_y(\bar{x}_i,t)\exp(-ik_x\bar{x}_i).$$

The Fourier transform $S(k_x,\omega)$ will be related to the quantity measured in a neutron scattering experiment.

We have evaluated $S(k_x,t)$ for values of k_x consistent with our system size and the periodic boundary conditions. For $k_x = 0$ and $\pi/2a$ there is a fairly rapid decay (see Fig. 3) but for $k_x = \pi/a$ we observe a much slower decay modulated at a period corresponding roughly to the mean reorientation time. The mean dipole moment of each sheet $\langle m_y(\bar{x})\rangle$ is shown in Fig. 4. One sees that our results are indeed consistent with a sinusoidal (antiferroelectric) variation of the sheet dipole moments in the a direction with a wavelength of $2a$. By extrapolation of the results of Ref. 4, we estimate that the wavelength of the critial fluctuations seen in the experiments would be about $3a$ at the temperature of our calculations. We have verified that this is the most significant order present in our simulations; for example, the amplitude of the spatial variations in $\langle m_x(\bar{x})\rangle$ are about 4 times smaller than $\langle m_y(\bar{x})\rangle$ and hence are probably not statistically significant.

In summary, we find that in our model individual anions are reorienting frequently (10–20 times each) during the course of our simulation. Nonetheless, there is a persisting (quasistatic) order along the a direction associated with the dipole moments of sheets of ions perpendicular to the a axis. The lifetime (Fig. 3) is certainly greater than the length of our simulation (3 ps). The quasistatic order that we observe (Fig. 3, inset, and Fig. 4) is best described as antiferroelectric order having a wavelength of twice the spacing in the a direction. It would be of interest to see if our predictions concerning the reorientation times, the nature of the coupled optic modes, and the antiferroelectric order can be confirmed by experiments.

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Approach to Melting in Ammonia as a Critical Transition

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The molar volumes of ammonia solid I and solid II were measured from 0.5 to 14.0 kbar and 185 to 320 K. Over regions that extend 3 kbar and 20 K into the solid phases, variations in compressibility and thermal expansion can be described by power laws with exponents similar to those usually associated with critical transitions. It is suggested that breaking of hydrogen bonds may account for the extreme softening of solid ammonia.

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Just before melting, many elements and compounds exhibit unusual behavior[1] marked by large increases in the isothermal compressibility,[2] $\kappa_T \equiv -V^{-1}(\partial V/\partial p)_T$, and in the isobaric thermal expansion,[3-5] $\alpha_p \equiv V^{-1}(\partial V/\partial T)_p$; large decreases in the frequency of low-lying phonon-libron modes[6]; and the vanishing of certain elastic constants.[7-8] These abnormal effects lead *a priori* to various kinds of instability in the solid.[9] We report here volumetric measurements that show that solid ammonia undergoes a dramatic softening on approach to melting. In the homogeneous solid phase, κ_T and α_p follow power laws indicative of a λ-type transition. We suggest that the wide range in p and T over which this behavior is observed makes ammonia an ideal subject for study of the anomalous effects that precede melting. Detailed knowledge about solid NH_3 is also needed to interpret data relating to planetary atmospheres.[10]

We used a piston-cylinder apparatus, designed for condensed gases,[11] to measure the p-V-T properties of 99.99% pure ammonia from about 185 to 320 K and 0.5 to 14.0 kbar. The phase diagram of condensed NH_3, along with experimental details, are given elsewhere.[12] Briefly, we found that the melting curve has two branches, as implied by the work of Vereshchagin and Voronov[13] and Hanson and Jordan.[14] The lower branch, bounding solid I, is given by

$$p_m(\text{I}) = 5.886\,[(T_m/T_{\text{g-l-I}})^{3.960} - 1], \tag{1a}$$

and the upper one, bounding solid II, is given by

$$p_m(\text{II}) = 11.156\,[(T_m/T_{\text{l-I-II}})^{1.516} - 1] + 3.070, \tag{1b}$$

where $p_m(\text{I, II})$ is the melting pressure in kilobars, T_m is the melting temperature in kelvins, $T_{\text{g-l-I}} = 195.48$ K is the gas-liquid-solid I triple-point temperature,[15] and $T_{\text{l-I-II}} = 217.34$ K is the liquid-solid I-solid II triple-point temperature. The two curves intersect at $p_m(\text{I, II}) = 3.070$ kbar, from which point a solid I-solid II transition line rises steeply in the p-T plane. We assume that ammonia solid I has a simple-cubic structure similar to that found in x-ray[16] and neutron-diffraction[17] studies made more than 20 K below $T_{\text{g-l-I}}$ at 1 bar. Solid II is thought to be face-centered cubic from preliminary x-ray measurements carried out in a diamond cell at room temperature.[18]

The molar volume of solid I was measured along five isotherms and three isobars to a distance of about 3 kbar and 20 K, respectively, from the melting curve, giving a total of 140 data points. For solid II we obtained 460 points along fourteen isotherms and seven isobars out to about the same distance from the melting line.

Several typical isotherms are shown in Fig. 1, where the upper experimental points represent liquid volumes V_l and the lower points represent solid-II volumes $V_s(\text{II})$. As the melting curve is approached from the solid side, $V_s(\text{II})$ undergoes a progressive enhancement that begins more than