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## A MOLECULAR DYNAMICS STUDY OF THE LATTICE VIBRATIONS OF SODIUM CHLORIDE

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**Résumé.** — Nous avons étudié par la méthode de la dynamique moléculaire numérique un système de 216 ions situés sur le réseau de NaCl et périodiquement répété. Pour les interactions de paires nous avons pris le potentiel proposé pour les ions rigides de NaCl par Tosi et Fumi. Les facteurs de structure dynamique et des autres propriétés ont été calculés pour les températures de 80, 302, 954 et 1 153 K. Les résultats sont comparés avec les prédictions de l'approximation quasi-harmonique.

**Abstract.** — The classical method of molecular dynamics has been used to study the properties of a periodically-repeating system of 216 ions in the NaCl-type lattice. For the interionic pair potential we adopt the rigid-ion model of Tosi and Fumi. Results are reported for the dynamical structure factor and other properties of NaCl at 80, 302, 954 and 1 153 K, and comparison is made with the predictions of quasi-harmonic lattice dynamics.

All the alkali-halide crystals melt at temperatures considerably greater than their Debye temperatures and may be treated as classical solids over much of their range of existence. The thermodynamics and lattice dynamics of the alkali halides in the solid state may therefore be studied by the established methods of computer simulation, either Monte Carlo [1] or molecular dynamics [2]. These computer *experiments* afford essentially exact solutions to the statistical mechanical problem for an assumed potential model. In this note we present selected results from an extensive molecular dynamics (MD) study of solid NaCl. We have used throughout the rigid-ion model of Tosi and Fumi [3], in which the pair potential is taken to be the sum of suitably parameterized Born-Mayer short-ranged interionic repulsions, London dispersion terms, and the usual coulombic interaction. More sophisticated models exist and

have been widely used, notably the deformation dipole model of Hardy [4], the shell model of Dick and Overhauser [5] and the breathing shell model of Schröder [6]. These models allow in differing ways for the effects on the dynamics of polarization of the ions, which results in a significant lowering of the frequencies of the optical modes of vibration. Despite this well-known limitation, the rigid-ion model remains one of the basic models of lattice dynamics. It plays much the same role for alkali halides as does the Lennard-Jones 12-6 potential for van der Waals solids; both simple models contain most of the essential physics of the true systems. Adams and McDonald [7] have recently used the Tosi-Fumi potentials to make extensive Monte Carlo studies of the equilibrium properties of 10 alkali halides in the NaCl structure. The systematic study of the *dynamics* of the rigid-ion NaCl model by the MD method therefore seems timely. The introduction of polarization poses considerable computational difficulties and we postpone a discussion of this problem

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TABLE I

Selected equilibrium quantities evaluated for NaCl using a system of 216 ions (with periodic boundary conditions) interacting with the Tosi-Fumi rigid-ion potential. Bracketed numbers are Monte Carlo results [7]

$T$ (K)	$V$ ( $\text{cm}^3 \cdot \text{mol}^{-1}$ )	$pV/NkT$	$-U$ ( $\text{kJ} \cdot \text{mol}^{-1}$ )	$\langle u_+^2 \rangle^{1/2}$ ( $\text{\AA}$ )	$\langle u_-^2 \rangle^{1/2}$ ( $\text{\AA}$ )	Time steps (100' s)
80.3	26.92	0.08	773.5	0.126	0.113	10
301.7	27.60	0.13	762.1	0.234	0.227	6
(298.0)	(27.65)	(0.0)	(762.6)			
953.8	29.50	0.87	727.3	0.494	0.460	10
(1 073.0)	(31.37)	(0.0)	(717.4)			
1 153.0	31.37	0.21	713.2	0.611	0.577	28.8

to a later paper. Here we only point out that it is not legitimate to use harmonic force models [4-6], valid only for a given lattice parameter, to make a MD study of the dynamics of a polarizable-ion crystal at different thermodynamic states.

There is, of course, an extensive literature on the theory of the lattice dynamics of alkali halides with particular emphasis on anharmonic effects as treated by perturbation theory [8, 9]. The most comprehensive study to date, by E. R. Cowley [10], showed that for the thermodynamic properties of NaCl the lowest-order perturbation theory was adequate up to about two thirds of the melting temperature. With this in mind we chose to carry out one MD run at 80 K, primarily to compare with quasi-harmonic lattice dynamics in a region where anharmonic effects should be small. We carried out another run at about room temperature (302 K), and two further runs at temperatures sufficiently high that anharmonic effects should be large (954 K, 1 153 K). The highest-temperature run was carried out at approximately the melting point of the model; this is higher than that of the real crystal (1 073 K).

Our system consisted of 108  $\text{Na}^+$  and 108  $\text{Cl}^-$  ions disposed on the interpenetrating fcc lattices of the NaCl crystal structure. Periodic boundary conditions were used, making it possible to employ the Ewald method in the calculation of the electrostatic energy. The classical equations of motion were solved using the algorithm of Verlet [12] with a time step of  $0.7 \times 10^{-14}$  s. A selection of data pertinent to the MD runs is given in table I. Thermodynamic properties agree well with those obtained by the Monte Carlo method [7]. In addition to the calculation of equilibrium quantities we computed the dynamical structure factor, in the manner of Levesque *et al.* [13], from the classical expression

$$\begin{aligned}
 S(\mathbf{Q}, \omega) &= \lim_{T \rightarrow \infty} \frac{1}{NT} \int_0^T e^{i\omega t} \rho_{\mathbf{Q}}(t) dt \times \\
 &\quad \times \int_0^T e^{-i\omega t'} \rho_{-\mathbf{Q}}(t') dt' \\
 &= \frac{1}{N} \lim_{T \rightarrow \infty} \frac{1}{T} |\rho_{\mathbf{Q}}(\omega)|^2
 \end{aligned} \quad (1)$$

$\mathbf{Q}$  and  $\omega$  are, respectively, the momentum and energy transfer and  $\rho_{\mathbf{Q}}(\omega)$  is the Fourier-Laplace transform of the density operator

$$\rho_{\mathbf{Q}}(t) = \rho_{\mathbf{Q}}^+(t) + \rho_{\mathbf{Q}}^-(t) \quad (2)$$

where, for example,

$$\rho_{\mathbf{Q}}^+(t) = \sum_{i \in +} e^{i\mathbf{Q} \cdot \mathbf{r}_i(t)} \quad (3)$$

$\mathbf{r}_i$  denotes the instantaneous position vector of the  $i$ th ion belonging to the  $\text{Na}^+$  sublattice. The evaluation of the dynamical structure factor thus reduces to the evaluation of partial dynamical structure factors :

$$S(\mathbf{Q}, \omega) = S_{++}(\mathbf{Q}, \omega) + S_{--}(\mathbf{Q}, \omega) + 2 S_{+-}(\mathbf{Q}, \omega). \quad (4)$$

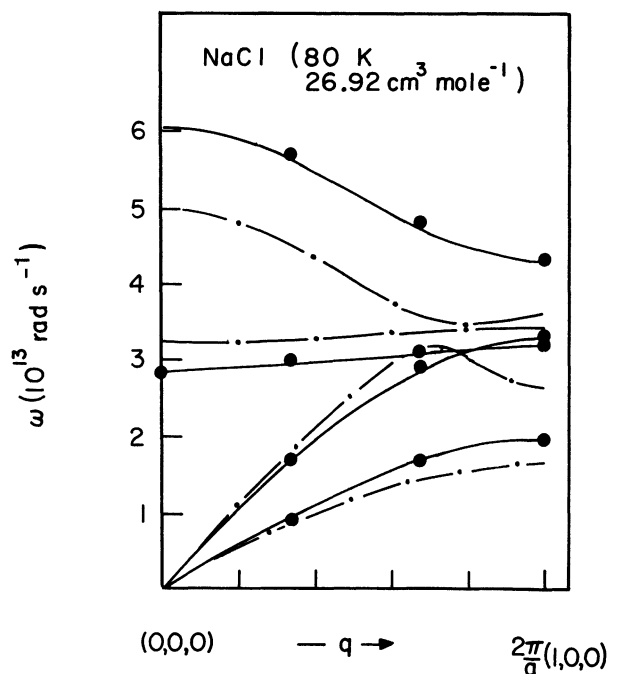


FIG. 1. — Phonon frequencies for the  $\langle 100 \rangle$  direction in NaCl at 80 K. The dash-dot curves are the experiment of Raunio *et al.* [11], the solid line shows the quasi-harmonic results for the Tosi-Fumi rigid-ion model, and the points indicate the peaks in  $S(\mathbf{Q}, \omega)$  for the same model.

The dynamical structure factor for the coherent inelastic scattering of neutrons can be constructed by weighting the partial quantities by the appropriate products of the nuclear scattering lengths. The one phonon approximation to  $S(Q, \omega)$  is given by the generalization to a two-component system of expressions due to Hansen and Klein [14]. During the MD run we evaluated both the full density operators and their one-phonon approximations.

We identify the phonon frequencies (energies) with the peaks in  $S(Q, \omega)$  derived from partial quantities weighted by the experimental neutron scattering lengths. Our results at 80 K for the  $\langle 100 \rangle$  direction are shown in figure 1. They are compared there with the quasi-harmonic values appropriate to the Tosi-Fumi rigid-ion model (E. R. Cowley, private communication) which were computed with the same mesh of points in the Brillouin zone as are consistent with the periodic boundary conditions in the MD calculations. The agreement is good, showing that the small size of system with which we are obliged to work does not lead to any serious errors in the phonon frequencies.

Figures 2 and 3 show two selected phonon at 80 K

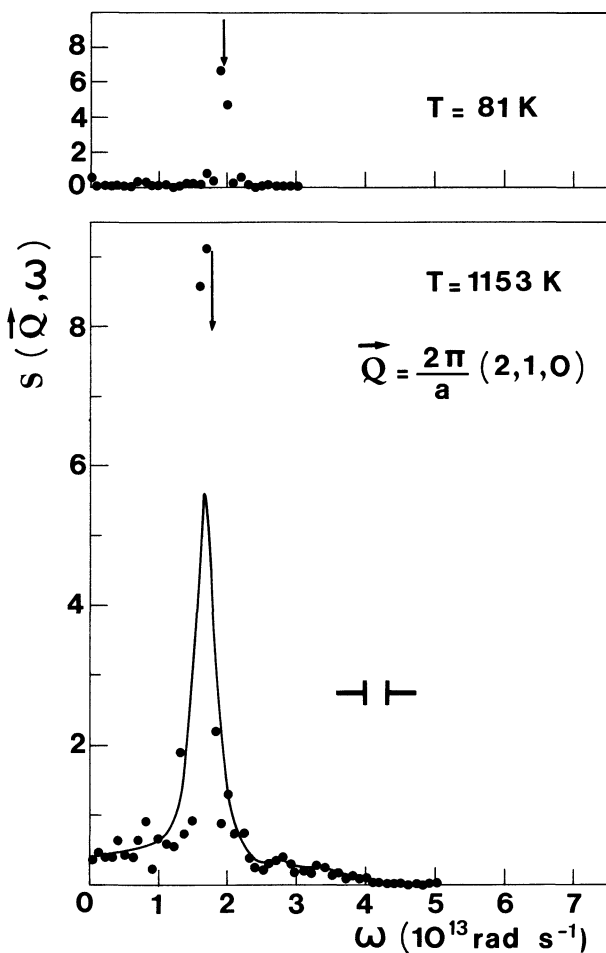


FIG. 2. — The calculated dynamical structure factor  $S(Q, \omega)$  for the zone-boundary TA phonon. The upper curve is for 80 K and the lower one for 1153 K. The arrows indicate the predicted peak positions for the Tosi-Fumi rigid-ion model in the quasi-harmonic approximation. The units of  $S(Q, \omega)$  are arbitrary.

and a temperature close to the near the melting point of the model. At 80 K the only feature presented by the computed  $S(Q, \omega)$  is the sharp phonon peak. At high temperature the phonons are still well-defined but the data show greater statistical noise and an appreciable anharmonic background. The noise can be reduced by convoluting the spectrum with a Gaussian filter of width  $\delta$ . This in turn is equivalent to truncating correlations in  $\rho_Q(t)$  beyond a time  $\tau = 2/\delta$ . The solid lines of figures 2 and 3 show the result of such a procedure using a width  $\delta = (3/2\pi)$  THz, equivalent to 600 time steps.

The transverse phonon exhibits a small negative anharmonic shift with respect to the quasi-harmonic

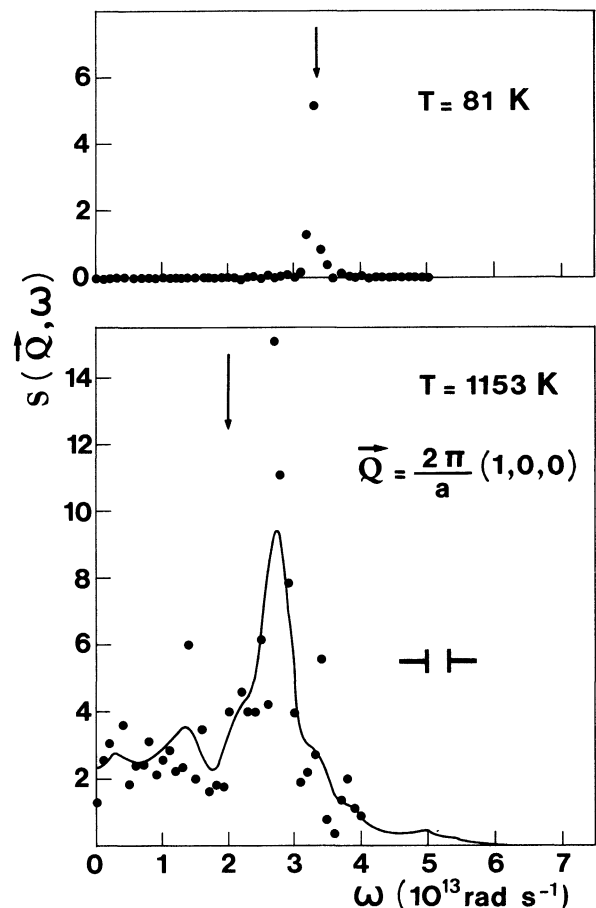


FIG. 3. — As figure 2, but for the zone-boundary LA phonon.

value while the longitudinal phonon shows a large positive shift. The explanation of qualitative differences such as these should provide a severe test of theories of anharmonicity. For each of these particular phonons, which correspond to relatively small  $Q$ -values, the one-phonon approximation was virtually indistinguishable from the full  $S(Q, \omega)$ . Unfortunately, we cannot make any detailed comparison with experiment, because no neutron scattering results are available for NaCl at very high temperatures. The transverse optic phonon ( $Q \rightarrow 0$ ) was found to have a large positive anharmonic shift

TABLE II

The % rms displacements  $\langle u^2 \rangle^{1/2}/d$  of  $\text{Na}^+$  and  $\text{Cl}^-$  ions for a system of 216 ions (with periodic boundary conditions) as calculated by MD and quasi-harmonic lattice dynamics (QH) for the Tosi-Fumi rigid-ion potential.

T (K)	d (Å)	$\langle u_+^2 \rangle^{1/2}/d$		$\langle u_-^2 \rangle^{1/2}/d$	
		MD	QH	MD	QH
80.3	2.817	4.5	4.0	4.0	3.8
301.7	2.840	8.2	7.8	8.0	7.6
953.8	2.904	17.0	15.4	15.8	14.8
1 153.0	2.964	20.6	19.0	19.5	18.5

compared with the quasi-harmonic value, in agreement with the calculations of E. R. Cowley [15]. However, although the temperature dependence agreed reasonably well with experimental results, the absolute value of the frequency of this mode was low compared with the measured infrared value of Mooij [16].

We observe finally that the MD values of the rms amplitudes of vibration of the ions are very large at high temperature but differ remarkably little from the quasi-harmonic results (see Table II). Our values are appreciably larger than those obtained for NaCl by Ree and Holt [17], who found from a cell model calculation that at zero pressure :

$$\langle u_+^2 \rangle^{1/2}/d = 6.16 \%,$$

$$\langle u_-^2 \rangle^{1/2}/d = 5.96 \%, \text{ at } 300 \text{ K};$$

$$\langle u_+^2 \rangle^{1/2}/d = 12.8 \%,$$

$$\langle u_-^2 \rangle^{1/2}/d = 12.5 \%, \text{ at melting point.}$$

(Note that  $d = \frac{1}{2} a$ .) The effects of correlations in the motion of neighbouring ions of the type neglected in a cell-model theory are therefore substantial even at room temperature. On the other hand our results are in close agreement with the calculations of Buyers and Smith [18] based on a deformation dipole model, showing that the effects of polarization are small. At high temperatures the values we find for the rms displacements are almost as large as those reported for typical quantum solids such as solid  $\text{He}^4$  and solid  $\text{H}_2$ .

Our calculations, taken together with the recently-reported work of Hansen and Klein [14] on rare-gas solids, demonstrate the power of the MD method in the study of lattice vibrations. A fuller account of the work will be published later in which a more detailed analysis of the anharmonic effects will be presented.

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