

## van der Waals forces in a Monte Carlo and lattice-dynamics study of the thermal and elastic properties of a rigid-ion model of potassium chloride

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We present benchmark calculations of the thermodynamic and elastic properties of a rigid-ion model of potassium chloride, at zero pressure, using a combination of Monte Carlo simulation at high temperatures (300–1000 K) and anharmonic lattice dynamics at low temperature (0–300 K). A new feature of our results is the fact that excellent agreement with the experimental results requires that, in contrast to the case of sodium chloride, the Born-Mayer repulsive interaction between nearest and third-nearest neighbors be supplemented by an attractive van der Waals interaction between second neighbors. We briefly discuss the problem of three-body forces.

### I. INTRODUCTION

In a recent paper,<sup>1</sup> we reported a calculation of the thermal and elastic properties of NaCl and compared our results with experiment. The calculation was based on anharmonic lattice dynamics up to room temperature and Monte Carlo simulations from there to the melting point. All the calculations were performed with care so that the results could serve as a benchmark for future work. The theory was based on a Born-Mayer potential whose two parameters were determined by the zero-degree volume and compressibility of the crystal, as well as the familiar, long-range Coulomb forces. We noted that Boyer<sup>2</sup> has shown that this potential, with very similar parameters, can be derived *ab initio*, using the density-functional method.

While agreement with experiment was remarkably good, there were, for some properties, deviations between theory and experiment outside their combined probable error. In part, we attributed this result to the neglect of three-body forces, based on the temperature dependence of the deviation from the Cauchy relations. But we also noted our neglect of like-neighbor potentials, e.g., for Cl—Cl, which was largely supported by the results of Boyer's calculations.<sup>2</sup>

The first theoretical work on ionic solids, the work<sup>3</sup> of Born and Landé on NaCl, which led directly to the discovery of quantum mechanics,<sup>4</sup> was, in principle, not very different from ours. Of course, we are able to do much more reliable calculations, for a wider range of temperatures, and to make a comparison with much more extensive and accurate data. But it is generally accepted that the rigid-ion model we are discussing here cannot account quantitatively for the high-frequency dielectric properties of alkali halides. Indeed, we believe that a more flexible model is needed to describe the optical properties of these solids. The first steps in this direc-

tion were taken by Dick and Overhauser<sup>5</sup> with the introduction of the shell model to allow for ionic polarizability. This work, including subsequent refinements, does give a quantitative account of some crystal properties, in particular, of the dispersion law measured by inelastic, coherent neutron scattering. A review of this work is given by Hardy<sup>6</sup> and by Bilz *et al.*<sup>7</sup> However, recent band-structure calculations,<sup>8</sup> as pointed out by Harrison,<sup>9</sup> suggest that the shell model's theoretical foundations must be seriously questioned. The ionic polarizability in the shell model arises from intra-ionic electronic transitions whereas the application of the band-structure calculations to the high-frequency dielectric constant suggests that the polarization effects that arise in alkali halides originate in interionic electronic transitions. These issues require further study.

It is, therefore, not surprising that there has been a recent resurgence of work on rigid-ion models.<sup>10</sup> All of this work has focused on Born-Mayer potentials for the repulsive part of the interaction. But it has also stressed the importance of the attractive van der Waals forces which we ignored in our work on NaCl.<sup>1</sup> In this work we will show that in KCl, with its much larger lattice spacing, the inclusion of van der Waals attractive forces between second-nearest neighbors (Cl—Cl) is essential to account for the thermal and elastic properties measured for KCl using a rigid-ion model. This is support for the same conclusion reached by Catlow *et al.*<sup>10</sup> who argued that the van der Waals constant for KCl obtained by Mayer<sup>11</sup> was much too small.

### II. RIGID ION POTENTIAL FOR KCl

Here we list the potential we have used to describe the short-range interactions between ions in KCl. For the nearest- and third-nearest neighbor cation-anion interaction we used

$$V = V_0 e^{-r/\rho} \quad (1)$$

with

$$V_0 = 8223.708 \times 10^{-12} \text{ erg} \quad (2)$$

and

$$\rho = 0.29713 \text{ \AA} \quad (3)$$

For the second-nearest-neighbor Cl—Cl interaction

$$V = -C/r^6, \quad (4)$$

with

$$C = 334.494 \times 10^{-60} \text{ erg cm}^6 \quad (5)$$

we assumed that the Born-Mayer term was absent for K—K and Cl—Cl forces and also that  $C=0$  for K—K second-nearest-neighbor interactions. The three parameters listed above were obtained from the crystal volume and the values of  $c_{11}$  and  $c_{44}$  at 0 K and  $P=0$ .

Initially, we used the potential of Eq. (1) with  $C=0$  and the two Born-Mayer parameters fitted to the lattice volume and the bulk modulus at  $T=0$ ,  $P=0$ , as in our work on NaCl.<sup>1,12</sup> We wanted to explore whether the ex-

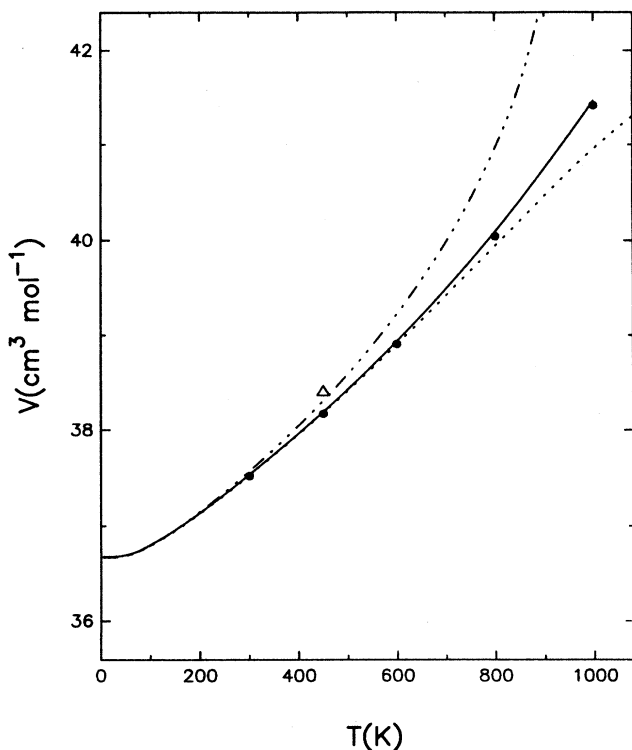


FIG. 1. Molar volume of KCl as a function of temperature at zero pressure; triangle, Monte Carlo simulation with  $4.0824 \times 10^6$  configurations without the van der Waals contribution to the rigid-ion potential; solid circles, Monte Carlo simulations with  $4.0824 \times 10^6$  configurations; dotted line, anharmonic lattice dynamics; dash-dotted line, quasiharmonic lattice dynamics; solid line, smoothed experimental data (Ref. 13).

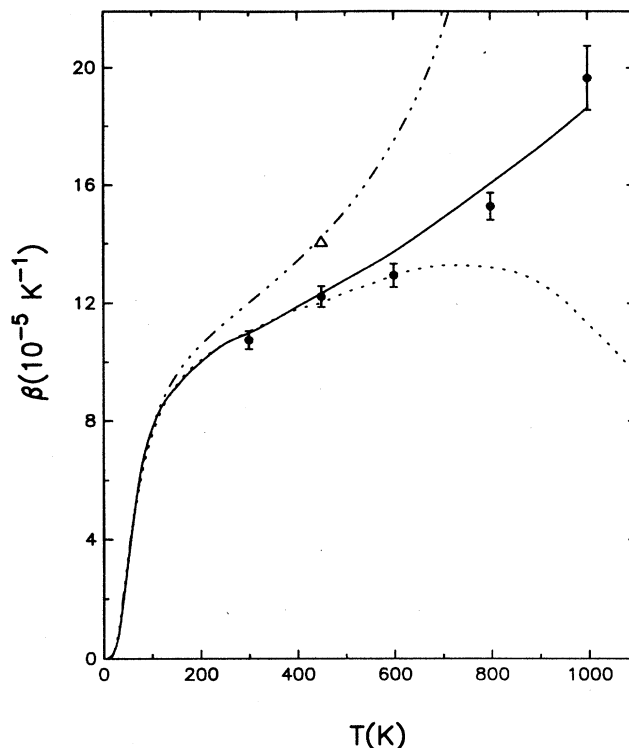


FIG. 2. Zero-pressure volume expansivity of KCl as a function of temperature; triangle, Monte Carlo simulation with  $4.0824 \times 10^6$  configurations without the van der Waals contribution to the rigid-ion potential; solid circles, Monte Carlo simulations with  $4.0824 \times 10^6$  configurations. The error bars represent one standard deviation of the mean due to purely statistical uncertainties. Dotted line, anharmonic lattice dynamics; dash-dotted line, quasiharmonic lattice dynamics; solid line, smoothed experimental data (Ref. 13).

cellent agreement with experiment for that substance also extended to KCl whose cell volume is 50% larger. Our results, shown as triangles on Figs. 1–8, are in striking disagreement with experiment for most but not all properties. It is at this point that we included van der Waals forces between second-nearest neighbor chlorine ions using Eqs. (1)–(4). This approach is supported by the work of Catlow *et al.* on rigid-ion interionic potentials in alkali halides.<sup>10</sup> They showed that the van der Waals constant for second-nearest-neighbor Cl—Cl interactions at  $P=0$  in KCl is surprisingly large, about five times that for second-nearest-neighbor K—K interactions. This contributes importantly to the region of the potential corresponding to the crystal volume reached in the temperature range we study. In NaCl (Refs. 1 and 12) the region of the potential sampled by the crystal is much closer to the minimum where the van der Waals interactions have been largely quenched by the repulsive overlap effects.

In our work on NaCl, the potential we derived by fitting experimental quantities was in good agreement with a potential calculated by Boyer,<sup>2</sup> using a local

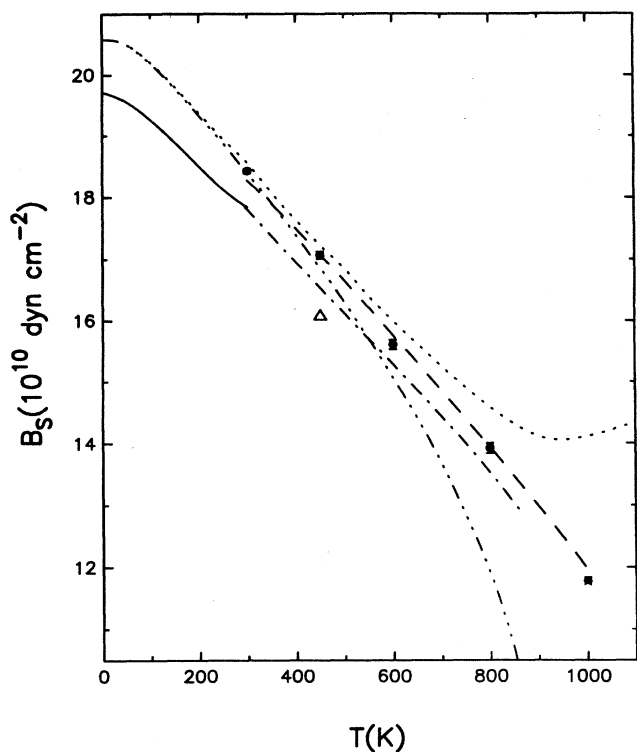


FIG. 3. Zero-pressure adiabatic bulk modulus of KCl as a function of the temperature; triangle, Monte Carlo simulation with  $4.0824 \times 10^6$  configurations without the van der Waals contribution to the rigid-ion potential; solid circles, Monte Carlo simulations with  $4.0824 \times 10^6$  configurations. The error bars represent one standard deviation of the mean due to purely statistical uncertainties. Dotted line, anharmonic lattice dynamics; dash-dotted line, quasiharmonic theory; solid line, smoothed experimental data (Ref. 14); dashed line, smoothed experimental data (Ref. 15); dash-dot line, smoothed experimental data (Ref. 16).

density-functional method. In the case of KCl, Boyer's potentials include a significant attractive component, which presumably corresponds approximately to the van der Waals potential. In the interest of simplicity, we have lumped all of these effects into a Cl—Cl force, and thus our fitted potential is not directly comparable with Boyer's.

### III. CALCULATION OF THERMAL AND ELASTIC PROPERTIES OF KCl

Our method for calculating the thermal and elastic properties of KCl is similar to that used in our work on NaCl.<sup>1,12</sup> At low temperatures we used anharmonic perturbation theory which overlaps nicely with our high-temperature Monte Carlo simulations at room temperature. For the latter we used a crystal with 216 atoms with periodic boundary conditions and about  $4 \times 10^6$  configurations. (See Tables I and II.) The Monte Carlo

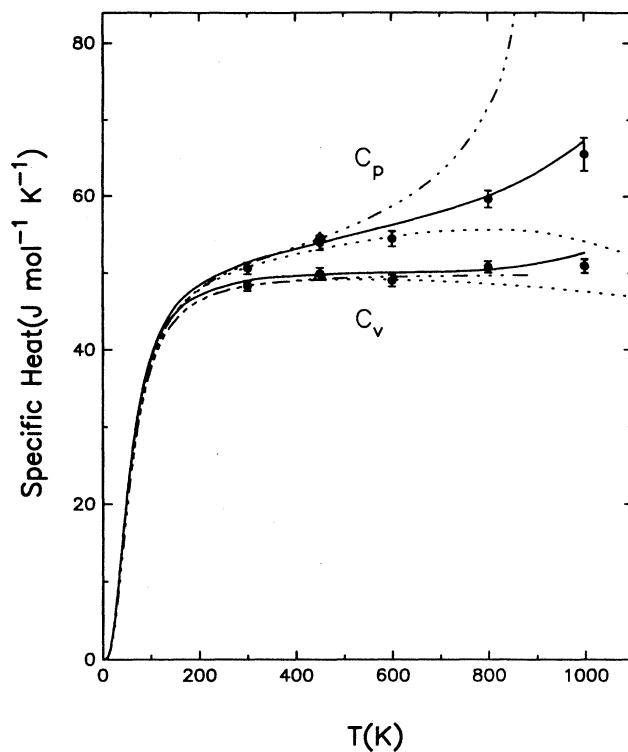


FIG. 4. Zero-pressure molar specific heat of KCl, at constant pressure and at constant volume, as a function of temperature; triangles, Monte Carlo simulations with  $4.0824 \times 10^6$  configurations without the van der Waals contribution to the rigid-ion potential; solid circles, Monte Carlo simulations with  $4.0824 \times 10^6$  configurations. The error bars represent one standard deviation of the mean due to purely statistical uncertainties. Dotted lines, anharmonic lattice dynamics; dash-dotted lines, quasiharmonic theory; solid lines, from smoothed experimental data (Refs. 17 and 18 for  $C_p$ ) (Refs. 13–20 for  $C_v$ ).

calculations were broken up into blocks of size  $5 \times 10^4$  configurations to enable us to obtain standard deviations for our results. In the real-space part of the Ewald summation for the Coulomb energy we included 256 neighbors within a distance of  $r_c = 3L/4$  from a given ion where  $L = 6a$  and  $a$  is the nearest-neighbor distance. The parameter  $\alpha$ ,<sup>21,22</sup> which divides the Ewald sum between real space and reciprocal space, was chosen<sup>10</sup> so that  $\alpha L = 5.05$ , and the reciprocal space sum was taken over 369 reciprocal lattice vectors for which  $0 < |\mathbf{n}|^2 \leq 1_c = 30$ . Our results are, therefore, of very high accuracy, superior to our earlier work on NaCl.

Whereas the results are unacceptable when van der Waals forces are omitted (triangular points), it is clear from our figures that the potential listed in Eqs. (1)–(4) leads to spectacular agreement with experiment along the zero-pressure isotherm. And this holds true for all properties at all temperatures. We point out that our work is based on a theoretical framework that is beyond reproach, in that the terms we have included in the potential are certainly there, and are important, and that we

TABLE I. The temperature dependence of zero-pressure thermodynamic functions for KCl. The uncertainty represents the standard error of the mean. All the Monte Carlo results correspond to  $4.0824 \times 10^6$  configurations. The results for  $u_x^2$  are quasiharmonic.

$T$ (K)	$V$ ( $\text{cm}^3/\text{mol}$ )	$P$ (bar)	$E$ ( $10^3 \text{ J/mol}$ )	$C_v$ (J/molK)	$C_p$ (J/molK)	$\gamma$	$\beta$ ( $10^{-5} \text{ K}^{-1}$ )	K	Cl
								$u_x^2$ ( $10^{-18} \text{ cm}^2$ )	
Anharmonic									
lattice									
0	36.671	0	-708.18	0	0	0.186	0	0.395	0.426
100	36.794	0	-706.33	37.63	38.05	1.473	7.54	0.773	0.813
200	36.950	0	-701.91	46.42	47.83	1.513	10.06	1.424	1.491
300	37.525	0	-696.93	48.34	50.78	1.513	11.04	2.137	2.237
Monte									
Carlo									
300	37.517	-4±9	-696.89±0.02	48.4±0.7	50.6±0.8	1.47±0.02	10.7±0.3	1.98±0.01	2.09±0.01
450	38.170	-10±18	-689.05±0.03	49.9±0.8	54.0±1.0	1.48±0.03	12.2±0.3	3.18±0.03	3.36±0.03
600	38.908	-25±28	-680.87±0.03	49.0±0.8	54.5±1.0	1.44±0.03	12.9±0.4	4.56±0.03	4.82±0.03
800	40.041	-36±36	-669.39±0.04	50.9±0.7	59.7±1.1	1.43±0.02	15.3±0.5	6.82±0.05	7.22±0.05
1000	41.416	-16±27	-657.05±0.04	51.0±0.9	65.5±2.2	1.46±0.04	19.6±1.1	9.82±0.04	10.37±0.04

TABLE II. Zero-pressure elastic functions for KCl as a function of temperature. The uncertainty represents the standard error of the mean. All the Monte Carlo results correspond to  $4.0824 \times 10^6$  configuration.

$T$ (K)	$B_T$	$B_S$	$c_{11}^T$	$c_{11}^S$ ( $10^{10} \text{ dyn/cm}^2$ )	$c_{12}^T$	$c_{12}^S$	$c_{44}$
Anharmonic							
lattice							
dynamics							
0	20.58	20.58	48.31	48.31	6.71	6.71	6.63
100	19.98	20.20	46.34	46.57	6.77	7.00	6.57
200	18.80	19.37	42.66	43.23	6.81	7.38	6.46
300	17.65	18.54	38.85	39.73	6.83	7.71	6.34
Monte							
Carlo							
300	17.60±0.06	18.42±0.04	39.29±0.04	40.12±0.05	6.75±0.09	7.58±0.06	6.372±0.009
450	15.79±0.05	17.07±0.06	34.2±0.1	35.5±0.1	6.60±0.06	7.87±0.06	6.15±0.01
600	14.0±0.1	15.61±0.08	29.4±0.1	30.9±0.1	6.4±0.1	8.0±0.1	5.92±0.02
800	11.9±0.1	13.92±0.08	23.4±0.1	25.5±0.1	6.1±0.2	8.1±0.1	5.55±0.02
1000	9.2±0.2	11.77±0.06	17.2±0.2	19.8±0.2	5.1±0.2	7.8±0.1	5.15±0.02

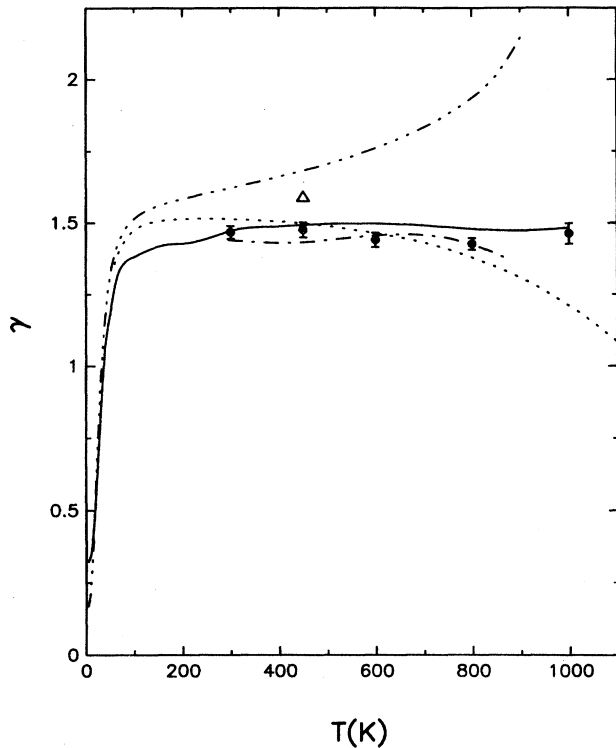


FIG. 5. Gruneisen's parameter  $\gamma$  for KCl, at zero pressure, as a function of temperature; triangle, Monte Carlo simulation with  $4.0824 \times 10^6$  configurations without the van der Waals contribution to the rigid-ion potential; solid circles, Monte Carlo simulations with  $4.0824 \times 10^6$  configurations. The error bars represent one standard deviation of the mean due to purely statistical uncertainties. Dotted line, anharmonic lattice dynamics; dash-dotted line, quasiharmonic theory; dashed-dot line, smoothed experimental data (Ref. 16); solid line, from smoothed experimental data (Refs. 18 and 20).

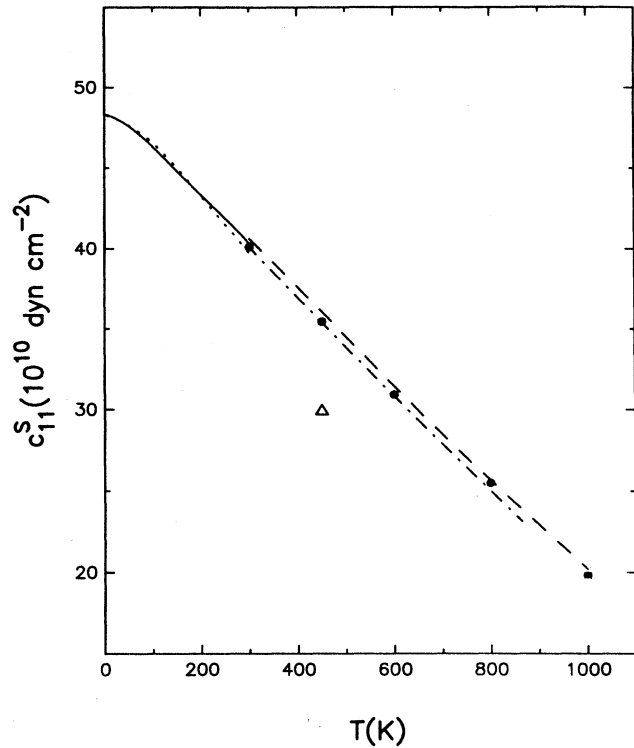


FIG. 6. Adiabatic elastic constant  $c_{11}^S$  as a function of temperature, at zero pressure; triangle, Monte Carlo simulation with  $4.0824 \times 10^6$  configurations without the van der Waals contribution to the rigid-ion potential; solid circles, Monte Carlo simulations with  $4.0824 \times 10^6$  configurations. The error bars represent one standard deviation of the mean due to purely statistical uncertainties. Dotted line, quasiharmonic theory; solid line, smoothed experimental data (Ref. 14); dashed line, smoothed experimental data (Ref. 15); dash-dotted line, smoothed experimental data (Ref. 16).

have used techniques which give numerically accurate results for this potential. We have neglected the effects of ionic polarizability and of three-body forces, but we believe that these will affect our results for the thermal and elastic properties only in detail. They may in fact be included to some extent in our model in an effective way because of our use of fitted parameters. Including a van der Waals term for large lattice parameters is given further support by our results. As for NaCl, the lattice dynamical calculations fail badly, as expected, at higher temperatures where perturbation theory diverges. By including the results of the quasiharmonic approximation, as well as those for a full anharmonic calculation including both cubic and fourth-order anharmonic corrections, we illustrate how perturbation theory fails as a function of temperature. A more detailed description of our theoretical procedures can be found in Ref. 7. We believe that a self-consistent theory is needed to cope with this problem. We plan to report on such work in a subsequent paper.

#### IV. CONCLUSION

The rigid-ion model for alkali halides continues to surprise us with its ability to account quantitatively for a wide range of experimental data on the thermodynamics and elasticity of these solids along the zero-pressure isotherm. We confirm this conclusion here for KCl. We found that for such an expanded solid, we had to supplement the Born-Mayer repulsion by a large van der Waals attractive term for second-nearest neighbor Cl—Cl interactions. This supports the ideas of Catlow *et al.*<sup>10</sup> The agreement between lattice dynamics and Monte Carlo simulations, on the one hand, and the experimental data, on the other hand, is excellent from 0 K to the melting point of KCl. We note that all the experimental elastic data are not in agreement with each other within their stated probable error. Thus a definitive test of the model must await a resolution of these experimental uncertainties. The large size of the van der Waals terms in the potential required for agreement with the experimen-

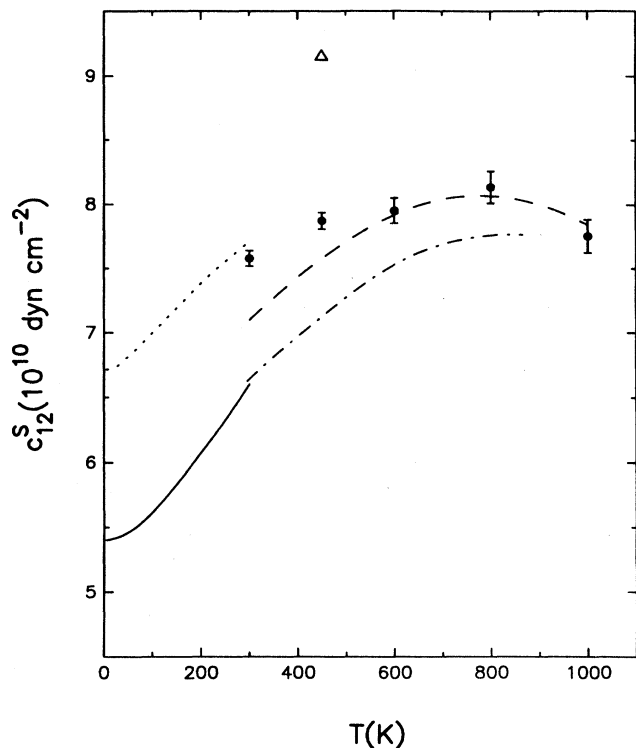


FIG. 7. Adiabatic elastic constant  $c_{12}^S$  as a function of temperature, at zero pressure; triangle, Monte Carlo simulation with  $4.0824 \times 10^6$  configurations without the van der Waals contribution to the rigid-ion potential; solid circles, Monte Carlo simulations with  $4.0824 \times 10^6$  configurations. The error bars represent one standard deviation of the mean due to purely statistical uncertainties. Dotted line, quasiharmonic theory; solid line, smoothed experimental data (Ref. 14); dashed line, smoothed experimental data (Ref. 15); dash-dotted line, smoothed experimental data (Ref. 16).

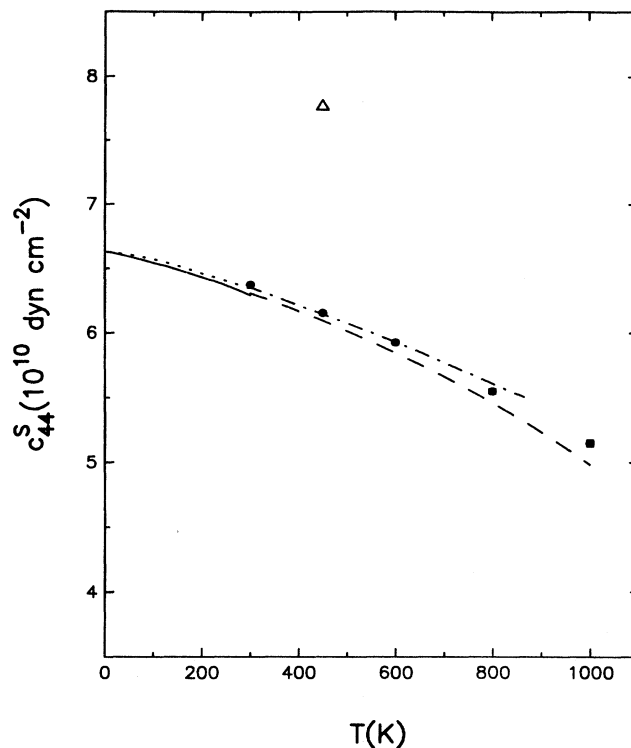


FIG. 8. Adiabatic elastic constant  $c_{44}^S$  as a function of temperature, at zero pressure; triangle, Monte Carlo simulation with  $4.0824 \times 10^6$  configurations without the van der Waals contribution to the rigid-ion potential; solid circles, Monte Carlo simulations with  $4.0824 \times 10^6$  configurations. The error bars represent one standard deviation of the mean due to purely statistical uncertainties. Dotted line, quasiharmonic theory; solid line, smoothed experimental data (Ref. 14); dashed line, smoothed experimental data (Ref. 15); dash-dotted line, smoothed experimental data (Ref. 16).

tal data is in agreement with the conclusions reached earlier by work on interionic potentials for alkali halides using 0 K experimental data.<sup>10</sup> Since we have not included any three-body forces in our potential, our theoretical results obey the Cauchy relations  $c_{12} = c_{44}$  for the static lattice at zero pressure. This is not observed experimentally. Experimentally,  $c_{12} \ll c_{44}$  at 0 K and  $P=0$ . As in NaCl, the deviation from the Cauchy relation changes sign close to room temperature which proves that there are explicit three-body forces which we have not included and that the deviation from the Cauchy relation is not merely due to anharmonicity. There is also a large contribution to the deviation from three-body forces at low temperatures which is of opposite sign.

Our work shows clearly that the quasiharmonic and lowest-order-anharmonic-theory approximations give results very different from each other and from the Monte Carlo values at high temperatures. It would be possible to adjust the potential so that it would give agreement with experiment for some properties and perhaps over a

limited range of temperature and pressures when used with one of the approximate methods, but this would clearly be misleading. As an example, we note that in Fig. 2, the thermal expansivity calculated by the Monte Carlo method for a model neglecting van der Waals forces happens to give the same result as a quasiharmonic calculation including van der Waals forces. Also, the quasiharmonic calculation will usually give good results for certain properties such as  $C_v$ . The only unambiguous procedure is to calculate a wide range of properties, using an accurate numerical technique. We believe we have accomplished this.

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