

## Lattice Dynamics with Three-Body Forces: Solid Xe and Kr

**Abstract:** Phonon dispersion curves, elastic constants, and the  $pV$  isotherms are calculated for solid Xe and Kr at 0 K using quasiharmonic lattice dynamics derived from multiparameter pair potentials. The computations account for the Axilrod-Teller-Muto three-body triple-dipole forces that arise in third-order perturbation theory. Approximate allowance is also made for anharmonic effects and, in the case of Xe, for three-body, third-order, dipole-quadrupole interactions and the three-body dipole interactions that arise in fourth-order perturbation theory. The over-all agreement with experimental phonon data is good except, in the case of xenon, for the lowest-energy phonons in the [110] direction. This has the consequence that the shear elastic constant  $(C_{11} - C_{12})/2$  and the zero temperature Debye theta are somewhat lower than current experimental values.

### Introduction

Experimental and theoretical studies of rare gases in solid, liquid, and gaseous states have provided an important testing ground for experimental and theoretical methods in physics. By determining interatomic potential energy functions from a limited amount of experimental data and using them to make theoretical predictions of the results of other experiments, it has been possible to compare results obtained by different experimental techniques and at the same time to test theoretical and computational methods. This has led to a far-reaching synthesis in which the same potential energy functions correlate data as diverse as, for example, molecular-beam scattering measurements, spectroscopic observations of vibrational levels of rare-gas dimers, and inelastic neutron scattering measurements of phonon-dispersion relations for rare gas crystals. The particular purpose of this paper is to use potential energy functions determined from other data to predict phonon dispersion curves for solid krypton and xenon. These curves are then compared with recent accurate measurements.

In a recent paper Barker et al. [1] have presented new pair potentials for the ground state of the inert gas dimers  $Kr_2$  and  $Xe_2$ . These interaction potentials were obtained by fitting an assumed analytic form to a wide variety of experimental gas phase data, including the dilute gas viscosity, second virial coefficients, vibrational level spacings of the dimers and differential collision cross sections, as well as the zero-temperature, zero-pressure lattice spacing in the solid. These pair potentials, and a new pair potential for xenon to be described in what follows, have the following form:

$$u(R) = \varepsilon[u_0(R) + u_1(R) + u_2(R) + u_3(R) + u_4(R)],$$

where

$$u_0(r) = \sum_{i=0}^5 A_i (r-1)^i e^{\alpha(1-r)} - \sum_{i=0}^2 C_{6+2i} / (\delta + r^{6+2i}),$$

and

$$u_1(R) = [P(r-1)^4 + Q(r-1)^5] e^{\alpha(1-r)}, \quad r > 1$$

$$= 0, \quad r < 1$$

$$u_n(R) = [F_n(r-s_n)^2 + G_n(r-s_n)^3] \exp[-\gamma_n(r-t_n)^2],$$

$$n = 2, 3, 4. \quad (1)$$

Here  $\varepsilon$  is the well depth and  $r = R/R_m$ , where  $R$  is the internuclear separation and  $R_m$  is this distance at the minimum of the potential. Theoretical estimates were used for the long-range coefficients  $C_{2i+6}$ . The potential parameters are given in Table 1.

The fit to gas phase data followed closely the method of Barker and Pompe [2], Bobetic and Barker [3], and Bobetic et al. [4]. In addition, however, the lowest vibrational level spacing was used to constrain the curvature of the pair potential near the minimum, while the old high-energy molecular beam data were abandoned in favor of a better fit to the newer high-temperature viscosity data. The differential collision cross sections were then used to determine precisely the well depth and the outer wall of the potential by varying the parameters  $\varepsilon$ ,  $P$ , and  $Q$ .

The lattice parameter of the solid was used to fix  $R_m$ . However, to do so it was necessary to allow for many-

Table 1 Parameters for interaction potentials for krypton and xenon.

Parameter	Potential			Parameter	Potential		
	Kr(K2) <sup>a</sup>	Xe(X3) <sup>a</sup>	Xe(X4) <sup>b</sup>		Kr(K2) <sup>a</sup>	Xe(X3) <sup>a</sup>	Xe(X4) <sup>b</sup>
$\epsilon/k(\text{K})$	201.9	282.35	282.35	$F_2$	0.0	2.08	2.08
$R_m(\text{\AA})$	4.0067	4.3623	4.3634	$G_2$	0.0	-6.24	-6.24
$A_0$	0.23526	0.2402	0.2402	$\gamma_2$	-	50.0	50.0
$A_1$	-4.78686	-4.8169	-4.8169	$s_2$	-	1.0	1.0
$A_2$	-9.2	-10.9	-10.9	$t_2$	-	1.0	1.0
$A_3$	-8.0	-25.0	-25.0	$\bar{F}_3$	0.0	0.0	-3.81
$A_4$	-30.0	-50.7	-50.7	$G_3$	0.0	0.0	0.0
$A_5$	-205.8	-200.0	-200.0	$\gamma_3$	-	-	100.0
$C_6$	1.0632	1.0544	1.0544	$s_3$	-	-	1.0
$C_8$	0.1701	0.1660	0.1660	$t_3$	-	-	0.87
$C_{10}$	0.0143	0.0323	0.0323	$F_4$	0.0	0.0	0.0
$\alpha$	12.5	12.5	12.5	$G_4$	0.0	0.0	-400.0
$\delta$	0.01	0.01	0.01	$\gamma_4$	-	-	150.0
$P$	-9.0	59.3	59.3	$s_4$	-	-	1.0
$Q$	68.67	71.1	71.1	$t_4$	-	-	0.7

<sup>a</sup>These pair potentials are derived by Barker et al. [1].  
<sup>b</sup>Present pair potentials; see text.

body forces in the solid. Following previous work it was assumed that the only many-body forces of importance were the long-ranged *three-body* forces. The potential energy in the solid can then be written as

$$E = \sum_{i>j} u(R_{ij}) + \sum_{i>j>k} u(R_i, R_j, R_k). \quad (2)$$

For krypton the Axilrod-Teller-Muto (ATM) triple-dipole interaction was the only three-body interaction considered. The third-order dipole quadrupole and fourth-order dipole interactions discussed by Doran and Zucker [5] appear to cancel one another to within the uncertainty of the estimates in their contributions to the properties of solid krypton. In the case of xenon, this cancellation is not so close and the contributions of these interactions were included, using the estimates given by Doran and Zucker [5]. Actually later work by Bell and Zucker [6] indicates that the Doran-Zucker estimate of the fourth-order dipole contribution is an excellent approximation to the contribution of dipole interactions in fourth and all higher orders of perturbation theory; thus we may regard our calculations as including these higher order contributions.

In the case of krypton we used the pair potential (K2; see Table 1) of Barker et al. [1], which gave very good agreement with all available experimental data. In the case of xenon, Barker et al. found that the potential X2 did not agree within experimental error with data on the vibrational levels of the xenon dimer, which became available too late to be incorporated into the main part of their work.

In a note added in proof they described another potential X3 (Table 1) which did agree with these data

within experimental error (Table 2). We have calculated  $pV$  data for this potential and find that the results are somewhat less satisfactory than for X2, as indicated in Fig. 1. We therefore derived another potential X4 (Table 1) which also agreed essentially within experimental error with the spectroscopic data but which gave improved agreement with the experimental  $pV$  data, even better than X2. This is shown in Fig. 1. Agreement was achieved by adding the term  $u_3$  of Eq. (1); at the same time we improved the fit of viscosities (Table 3) by adding the term  $u_4$  of Eq. (1). This potential X4 also gave an excellent fit of the differential scattering cross sections of Barker et al. [1], i.e.,  $\chi^2 = 0.041$ , as compared with 0.054 for X2 and 0.038 for X3, and of second virial coefficients [7], including new low-temperature measurements [8]. For the cohesive energy of crystalline xenon at 0 K, X4 gave -3773 cal/mole compared with the experimental [9] value  $-3786 \pm 22$  cal/mole. By comparison, X2 gave -3754 cal/mole and X3 -3770 cal/mole. Thus X4 gives an excellent fit of available experimental data, and this potential is used in the calculations described in this paper.

#### Lattice dynamics of Xe at 0 K

The basic theory of the lattice dynamics of the gas crystals in the presence of three-body forces has been given in earlier papers [3, 10-12]. Here we carry out a quasi-harmonic calculation of the phonon frequencies,  $\omega_{q\lambda}$  including explicitly in the dynamical matrix the third-order triple-dipole forces [3]. Anharmonic effects were incorporated by an approximate frequency-shift method [10]. This method was tested and found to be adequate [11]

**Table 2** Vibrational level spacings for Xe<sub>2</sub>; experimental and calculated values.

Level spacing no., $v$	$\Delta G_{v+1/2}(\text{expt})^a$	$\Delta G_{v+1/2}(X2)$	Calc-expt differential	$\Delta G_{v+1/2}(X3)$	Calc-expt differential	$\Delta G_{v+1/2}(X4)$	Calc-expt differential
0	19.90	19.23	-0.67	19.73	-0.17	19.61	-0.29
1	18.55	18.08	-0.47	18.47	-0.08	18.38	-0.17
2	17.20	16.94	-0.26	17.18	-0.02	17.12	-0.08
3	16.17	15.79	-0.38	15.89	-0.28	15.85	-0.32
4	14.63	14.68	0.05	14.66	0.03	14.64	-0.01
5	13.70	13.56	-0.14	13.47	-0.23	13.45	-0.25
6	12.63	12.44	-0.19	12.35	-0.28	12.34	-0.29
7	11.33	11.35	0.02	11.25	-0.08	11.26	-0.07
8	10.15	10.25	0.10	10.19	0.04	10.21	0.06
9	8.95	9.20	0.25	9.15	0.20	9.18	0.23

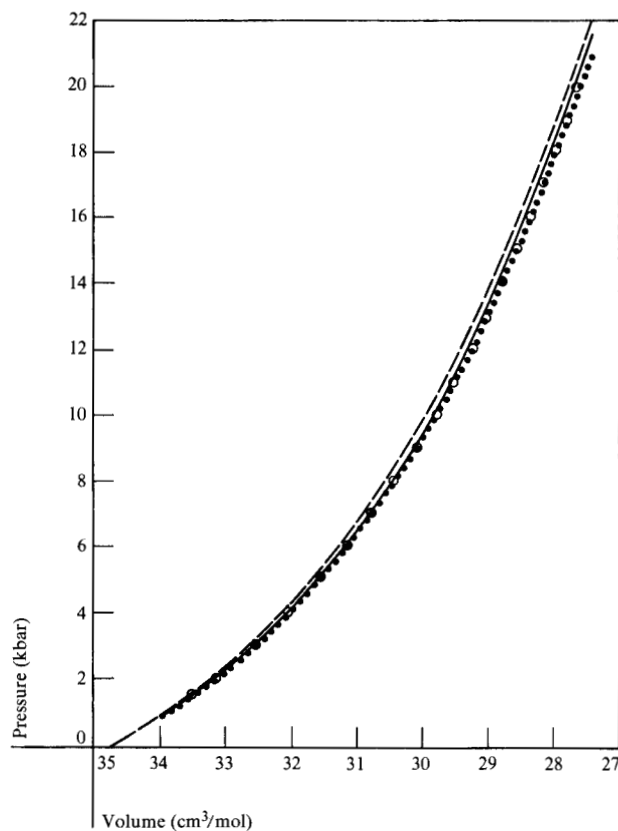
<sup>a</sup>D. E. Freeman, K. Yoshino, and Y. Tanaka, *J. Chem. Phys.* **61**, 4880 (1974). Units are cm<sup>-1</sup>. The estimated experimental error is  $\pm 0.3$  cm<sup>-1</sup>.

for solid Ar at 0 K and so should be even better here where anharmonic effects are considerably smaller. In this approach the quasiharmonic frequencies are first used to obtain the velocity of sound  $v(q\lambda) = (\partial\omega_{q\lambda}/\partial q)_{q \rightarrow 0}$  and hence the elastic constants, since, for example,

$$\rho v(100L)^2 = C_{11}, \rho v(100T)^2 = C_{44},$$

$$\rho v(110T_1)^2 = (C_{11} - C_{12})/2, \text{ etc.},$$

**Figure 1** Pressure-volume relationship for solid xenon near 0 K. Solid curve, X2; dashed curve, X3; dotted curve, X4; circles, experimental data of Anderson and Swenson [18].



where  $\rho$  is the crystal density. The elastic constants calculated in this fashion include the usual two-body "lattice" contribution as well as the triple-dipole "lattice" contribution  $C_{ij}(DDD)_3$  but not the anharmonic contribution due to the vibrational (zero-point) energy,  $C_{ij}(\text{anhc})$ . The latter are calculated from the strain dependence of the second and fourth moments of the phonon frequency spectrum using the method of Barron and Klein [13], and values are given in Table 4. The contribution from higher order three-body forces to the elastic constants are estimated from the work of Doran and Zucker [5] in the following way. Doran and Zucker evaluated the appropriate three-body lattice sums, and hence estimated  $E(DDD)_3$ ,  $E(DDQ)_3$ ,  $E(DQQ)_3$ , and  $E(DDD)_4$ . Since these energies are volume dependent, being proportional respectively to  $V^{-3}$ ,  $V^{-11/3}$ ,  $V^{-13/3}$ , and  $V^{-4}$ , their contribution to the pressure  $p = -(\partial E/\partial V)$  and bulk modulus  $B = -V(\partial p/\partial V)$  is readily determined. Moreover, it turns out that the contribution of  $u(DDD)_3$  to shear elastic constants is negligible [11] (essentially because shear modes propagate with no first-order change in the crystal volume) and hence the relationship  $3B = (C_{11} + 2C_{12})$  is sufficient to determine the contribution of  $u(DDD)_3$  to the individual elastic constants, namely,

$$B(DDD)_3 \approx C_{11}(DDD)_3 \approx C_{12}(DDD)_3;$$

$$C_{44}(DDD)_3 = 0.$$

If we make the Ansatz that the above relationships also hold for the other three-body interactions discussed above, then their contributions to the individual elastic constants are also determined by the calculations of Doran and Zucker. Values calculated in this fashion are given in Table 4. It is seen there that these higher order three-body effects to some extent cancel the anharmonic contributions. Because of this, it is not worth while to include explicitly either the anharmonic effects or these

**Table 3** Viscosity of gaseous Xe.

$T(K)$	$\eta(expt)^a$ $\mu\text{poise}$	$\eta(calc X4)$ $\mu\text{poise}$	Percent difference	$T(K)$	$\eta(expt)^a$ $\mu\text{poise}$	$\eta(calc X4)$ $\mu\text{poise}$	Percent difference
200	155.8	156.3	-0.3	900	600.9	599.5	0.2
300	232.4	232.3	0.0	1000	649.4	648.3	0.2
400	305.8	305.0	0.3	1100	695.4	694.8	0.1
500	373.9	372.6	0.3	1200	739.3	739.3	0.0
600	436.7	435.3	0.3	1300	781.3	782.0	-0.1
700	495.1	493.5	0.3	1400	821.6	823.2	-0.2
800	549.7	548.1	0.3	1500	860.4	863.1	-0.3

<sup>a</sup>G. C. Maitland and E. B. Smith, *The Viscosities of Eleven Common Gases; A Critical Compilation*, Physical Chemistry Laboratory, Oxford, 1971.

higher order three-body forces into the lattice dynamics. Instead, we assume that it is sufficient to normalize the quasiharmonic frequencies derived from the pair potential plus  $u(DDD)_3$  by the  $q$ -independent factor  $[1 + (\Delta C_{ij}/C_{ij})]$ , where  $\Delta C_{ij} = C_{ij}(anhc) + C_{ij}(DDD)_4 + C_{ij}(DDQ)_3 + C_{ij}(DQQ)_3 + C_{ij}(QQQ)_3$ . The combined effect of these terms is never more than about one percent. Phonon dispersion curves calculated in this fashion are shown in Fig. 2, where they are compared with recent experimental data [15, 16] measured at 10 K. Agreement is good everywhere except for the low frequencies of the lowest branch in the [110] direction, for which the calculated values are lower than experiments. As a consequence of this the calculated value of  $(C_{11} - C_{12})/2$  is lower than the value derived from the neutron data. We see in Table 2 that the theoretical value of the zero-temperature Debye theta is also lower than the experimental value [17]. On the other hand the calculated and experimental values of  $C_{44}$  agree very well. Also the initial slope of the transverse branch in the [111] direction, which depends solely on these two shear constants, is well fitted by theory, as shown in Fig. 2.

The calculated  $pV$  isotherm for solid Xe at 0 K is shown in Fig. 1, where it is compared with the recent data of Anderson and Swenson [18]. The agreement between theory and experiment is excellent over the whole range of the data. From their data Anderson and Swenson derived a value of 36.5 kbar for the bulk modulus at zero pressure, i.e.,  $B = -V(\partial p/\partial V)_{p \rightarrow 0}$ . Our theoretical value is calculated to be 39.3 kbar (Table 4). It is particularly surprising that these two values are so different because the original  $pV$  data from which Anderson and Swenson extrapolate their value are well fitted by the theory. The theoretical value for  $B$  agrees better with a recent direct measurement of Korpiun et al. [19], who found  $B = 37.9 \pm 0.5$  kbar.

We summarize our findings. Our model for solid Xe predicts values of  $\Theta_0$  and  $(C_{11} - C_{12})/2$  somewhat lower than experimental values. However the calculated transverse phonons in the [111] direction which at low  $q$  de-

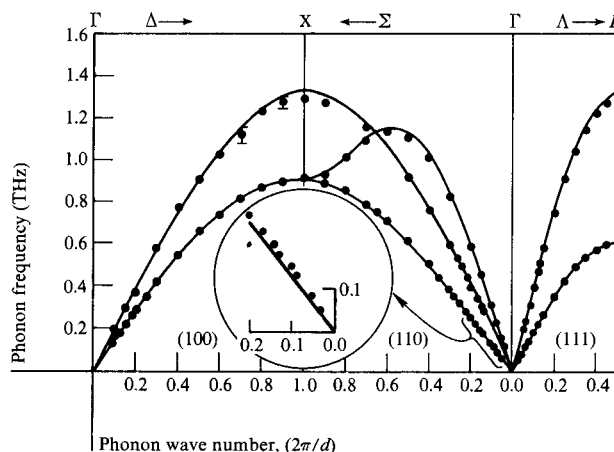
pend upon these same elastic constants agree well with experiment. The zero pressure bulk modulus which is the limiting slope of the  $pV$  isotherm is calculated to be greater than either the value derived from an analysis of neutron scattering data [15, 16] or that extrapolated from the  $pV$  data; yet the  $pV$  isotherm itself fits well. The zero-pressure bulk modulus does, however, agree rather better with another independent experimental value [19].

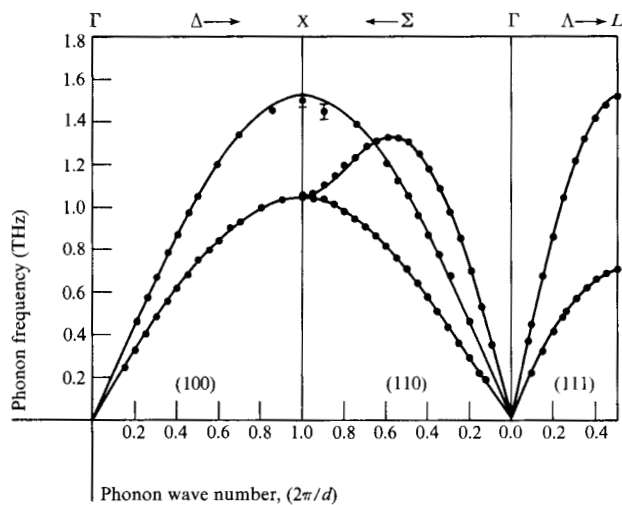
It seems to us unlikely that any changes in the pair potential or in the model for the many-body forces will remove all of these inconsistencies.

**Lattice dynamics of Kr at 0 K**

The phonon dispersion curves are calculated for Kr at 0 K using the same methods as outlined in the previous section, except that the higher order three-body forces other than ATM are ignored for reasons already discussed. Our results in Fig. 3 are compared with the experimental 10 K data of Skalyo et al. [20]. The overall

**Figure 2** Phonon dispersion curves for solid xenon. Solid curves, calculated for potential X4 with many-body interactions (0 K). Points, experimental data of Lurie et al. [15, 16] (10 K). Inset shows lowest [110] branch on enlarged scale.





**Figure 3** Phonon dispersion curves for solid krypton. Solid curves, calculated (0 K); points, experimental data of Skalyo et al. [20].

**Table 4** Elastic constants (in kbar) for solid Xe at 0 K.

	$C_{ij}(\text{total}, X^A)$	$C_{ij}(\text{expt})$	$C_{ij}(\text{anhc})$	$\Delta C_{ij}$
$C_{11}$	54.5	$52.7 \pm 0.9^a$	0.9	-0.4
$C_{12}$	31.7	$28.2 \pm 0.8^a$	0.7	-0.6
$C_{44}$	29.7	$29.5 \pm 0.4^a$	0.4	0.3
$B^A$	39.3	$36.4 \pm 0.8^a$	0.8	-0.5
		$36.5^b$		
		$37.9 \pm 0.5^c$		
$A$	2.61	$2.41^d$		
$\Theta_0(\text{K})$	61.0	$62.5 \pm 1.1 \text{ K}^a$		
		$64.0 \pm 1.0 \text{ K}^d$		

<sup>a</sup>Value derived from neutron scattering measurements at 10 K. N. A. Lurie, G. Shirane, and J. Skalyo [15, 16].

<sup>b</sup>Value derived from analysis of high pressure data. M. S. Anderson and C. A. Swenson. [18].

<sup>c</sup>Direct measurement from low pressure  $pV$  data. P. Korpiun et al. [19].

<sup>d</sup>Value taken from analysis of  $C_p$  data. H. Fenichel and R. Serin [17].

**Table 5** Elastic constants (in kbar) of solid Kr at 0 K

	$C_{ij}(\text{total})$	$C_{ij}(\text{expt})$	$C_{ij}(\text{anhc})$
$C_{11}$	49.9	$51.4 \pm 0.6^a$	1.8
$C_{12}$	28.6	$28.4 \pm 0.6^a$	1.3
$C_{44}$	26.9	$26.8 \pm 0.3^a$	0.7
$B^A$	35.7	$36.1 \pm 0.5^a$	1.5
		$33.4^b$	
		$34.5 \pm 0.4^c$	
$A$	2.52	$2.33 \pm 0.05^d$	
$\Theta_0$	71.1 K	$71.9^d$	
		$71.7 \pm 0.7^e$	

<sup>a</sup>Values derived from neutron scattering data at 10 K [20].

<sup>b</sup> $pV$  data (see ref. [15]) at 4.2 K.

<sup>c</sup>X-ray data, A. O. Urvas, D. L. Losee, and R. D. Simmons, *J. Phys. Chem. Solids* **28**, 2267 (1967).

<sup>d</sup>From analysis of  $C_p$  data, L. Finegold and N. E. Phillips, *Phys. Rev.* **177**, 1383 (1969).

<sup>e</sup>From analysis of  $C_p$  data, R. H. Beaumont, H. Chihara, and J. A. Morrison, *Proc. Phys. Soc. (London)* **78**, 1462 (1961).

agreement is very good. The elastic constants are given in Table 5; the agreement with experiment is better than for solid Xe. The  $pV$  isotherm agrees [1] with experiment about as well as for solid Xe, and again the experimentally extrapolated bulk modulus [18] appears to be a little low.

## Discussion

For solid Xe it is necessary to allow for higher order contributions to the three-body energy than the customary triple-dipole term  $(DDD)_3$  that arises in third-order perturbation theory [5, 6]. One must also include dipole-quadrupole terms that arise in third order as well as the three-body fourth-order term  $(DDD)_4$ . Thus we have for Xe, but not for Kr,

$$u(R_i, R_j, R_k) \approx u(DDD)_3 + u(DDQ)_3 + u(DQQ)_3 + u(QQQ)_3 + u(DDD)_4, \quad (3)$$

We stress that all these terms are three-body contributions. Doran and Zucker [5] have shown that for solid Ne the last four terms are numerically small, while fortuitously for solid Ar and Kr they almost cancel. In solid Xe the over-all effect of these higher order terms is to reduce the effect of  $u(DDD)_3$  slightly.

In this paper we have presented calculations of properties of solid Xe and Kr other than those that were used in fitting the pair potential. The calculations thus serve as a consistency check on our model for the forces in these solids.

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