PHYSICAL REVIEW B VOLUME 1, NUMBER 6 15 MARCH 1970

Calculations of the Grüneisen Parameter for Some Models of the Solid*

Albert C. Holt and Marvin Ross
Lawrence Radiation Laboratory, University of California, Livermore, California 94550

(Received 23 September 1969)

Using a fixed interatomic potential function, we calculate values of the Grüneisen parameter by means of five computational models. The models compared are Monte Carlo, Lennard-Jones-Devonshire cell model, lattice dynamics, Dugdale-MacDonald, and Slater. The last three models use the harmonic form of the intermolecular potential, while the first two use the full form. Consequently, some conclusions can be drawn on the importance of anharmonic forces in rare-gas crystals.

I. INTRODUCTION

THE Grüneisen parameter γ, defined as

$$\gamma=\frac{V}{C_V}\left(\frac{\partial P}{\partial T}\right)_V \tag{1a}$$

or

$$\gamma=V\left(\frac{\partial P}{\partial E}\right)_V, \tag{1b}$$

is an extremely useful quantity in high-pressure physics. This parameter allows the extraction of a maximum of information from a minimum of data, which is a special virtue for experimental conditions where data are often difficult to obtain. In practice,[1] *a* and *b* are approximated by the use of the Grüneisen equation of state,[2]

$$\gamma\doteq V\frac{(\Delta P)_V}{(\Delta E)_V}, \tag{2}$$

where the quantities $(\Delta P)_V$ and $(\Delta E)_V$ are changes in pressure P and internal energy E at constant volume, and γ is usually assumed to be a function of V only. Thus, from a knowledge of the Grüneisen parameter, an isotherm at one temperature can be made to supply additional neighboring isotherms. To obtain the Grüneisen parameter, P, E or P, T information is needed at more than one temperature. However, for systems under very high pressures and temperatures this information is generally at a premium, and it is for this reason that the Grüneisen parameter was desired in the first place. Because the Grüneisen parameter is such a useful quantity and is so difficult to obtain experimentally, a considerable amount of theoretical effort has been expended in its calculation.[3] A theoretical model requires specific assumptions about the interatomic forces and the nature of the solid at high pressure. The correctness of the model is then tested by comparison of prediction with experiment. However, since very little experimental data are available, the theoretical situation must necessarily be unclear.

The purpose of the present paper is to present calculations of pressure and the Grüneisen parameter for a number of equations-of-state models and compare these results with those of the Monte Carlo method which is, in principle, an exact method of generating the thermodynamic properties of a solid. In this method, the atoms are assumed to interact by some specified interatomic potential. Periodic boundary conditions are used, and the atoms are moved about by using a well-established procedure.[4] The averages over these moves or Markov chain gives the ensemble averages and thermodynamic properties of the model systems. In a previous publication,[5] Monte Carlo isotherms for solid argon were published using a pairwise additive intermolecular potential that was obtained from an analysis of high-pressure experiments in which liquid argon was shock compressed to 365 kbar and a density twice that of the liquid.

This potential was of the form

$$\phi(r)=\epsilon\left\{\left(\frac{6}{\alpha-6}\right)\exp\left[\alpha\left(1-\frac{r}{r^*}\right)\right]-\left(\frac{\alpha}{\alpha-6}\right)\left(\frac{r^*}{r}\right)^6\right\}, \tag{3}$$

where

$$\alpha=13.5\,,\quad r^*=3.85\ \text{Å},\quad \text{and}\quad \epsilon/k=122.0°\text{K}.$$

Using the method outlined in the next section it is also possible to calculate the Grüneisen parameter. The values of the pressure and Grüneisen parameter calculated by the Monte Carlo method involve no approximations other than those of the Monte Carlo method. Consequently, because we know the exact form of the intermolecular potential, it becomes possible to provide a detailed check of approximate theories which calculate the pressure and the Grüneisen parameter. Using this same intermolecular potential, we have calculated these properties by means of lattice dynamics,[6] the Lennard-Jones-Devonshire model,[7] and the equations

---

* Work performed under the auspices of the U. S. Atomic Energy Commission.

[1] M. H. Rice, R. G. McQueen, and J. M. Walsh, Solid State Phys. **6**, 1 (1958).

[2] If Eq. (1) is taken as the definition of γ then Eq. (2) is strictly valid only if γ is independent of E.

[3] C. G. Horton, Am. J. Phys. **36**, 93 (1968). This review article contains extensive references to the more recent work on lattice dynamics and on the Grüneisen parameter for rare-gas crystals.

[4] W. W. Wood and F. R. Parker, J. Chem. Phys. **27**, 720 (1957).

[5] M. Ross and B. Alder, J. Chem. Phys. **46**, 4203 (1967).

[6] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, London, England, 1964).

[7] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954).

of Dugdale and MacDonald[1] and Slater.[1] We have compared these results to those of the Monte Carlo calculations for the same potential. The method of lattice dynamics is also an exact method but for the harmonic approximation of the pair potential. Consequently, for the harmonic form of the potential [Eq. (3)], we have calculated by lattice dynamics the pressure and γ for the same system as in the Monte Carlo calculations, which used the full potential, and can thereby evaluate the importance of the anharmonic corrections to these properties. The calculations for these models are described in Sec. II, and the results are discussed in Sec. III. All the calculations described in Sec. II were made in the context of classical physics, and as such are strictly valid for high temperature.

II. CALCULATIONS

In this section, we outline the methods used in making the calculations for the various models. These calculations were made as a function of volume to high compression using a pairwise additive intermolecular potential. For the limiting case of infinite compression, the idea of a pairwise additive intermolecular force loses its usual meaning. This is true because when an inert gas is compressed along an isotherm to extreme densities, the energy gap between the filled valence and empty conduction bands will disappear at some volume, the system will become metallic, and the valence electrons will no longer be in closed shells but will move almost freely in a conduction band. One of us[8] has shown that this transition to metallic behavior occurs at about 12 cc/mole for xenon and 4.5 cc/mole for argon. Consequently, in the limit of extreme compression, the system must be regarded as a system consisting of a uniformly distributed electron gas and positive ions rather than a system of neutral atoms. In this limit ($V \rightarrow 0$) Kopyshev[9] has shown that the effect of the screening of the nuclei by the electrons becomes negligible and that the limiting value of γ is $\frac{1}{2}$. The limiting behavior may also be seen from an alternative point of view. The most likely limiting form of the pairwise intermolecular repulsive force[10] is $\phi(r) \approx e^{-\alpha r}/r$. At normal densities the exponential dominates, and for simplicity $1/r$ is considered a constant. But in the limit of $V \rightarrow 0$, $\phi(r) \approx 1/r$. For the harmonic solid, with ions interacting by means of a $1/r^n$ potential, $\gamma = \frac{1}{6}n + \frac{1}{3}$ so that the value of γ at extreme compressions will be $\frac{1}{2}$, in agreement with Kopyshev. Accordingly, we calculate γ for each of the models down to a volume of 5 cc/mole and then extrapolate to $\gamma = \frac{1}{2}$.

Monte Carlo

Inasmuch as pressures and energies over a wide range of conditions have already been reported for this potential, it will suffice here to detail only the calculations of the Grüneisen parameter. This was done by calculating C_V and $V(\partial P/\partial T)_V$ separately for each 5000 or 10 000 configurations and using Eq. (1a) to obtain γ over this range. The γ's shown in Table I and Fig. 1 represent an average γ over approximately 300 000 configurations. The error estimate represents the standard deviation of these results. The expressions for C_V and $V(\partial P/\partial T)_V$ are

$$C_V/Nk = N\left[\left\langle\left(\frac{U}{RT}\right)^2\right\rangle - \left(\frac{\langle U\rangle}{RT}\right)^2\right] + 1.5 \tag{4}$$

and

$$\frac{V}{Nk}\left(\frac{\partial P}{\partial T}\right)_V = 1 + N\left[\left\langle\left(\frac{U}{RT}\right)\left(\frac{PV}{RT}-1\right)\right\rangle - \left\langle\left(\frac{U}{RT}\right)\right\rangle\left\langle\left(\frac{PV}{RT}-1\right)\right\rangle\right], \tag{5}$$

where we have used the notation of Wood[3] whose paper provides the details for the Monte Carlo calculations. The $\langle\ \rangle$ in these equations indicate the ensemble or Markov chain averages, and N is the number of particles in the Monte Carlo calculation. In our calculations N was 108. The quantity U is the total potential energy of a configuration and is given by

$$U = \sum_{i>j} \phi(r_{ij}).$$

The compressibility of a configuration is given by

$$\left(\frac{PV}{RT}\right) - 1 = -\frac{1}{6NkT}\sum_{i>j} \mathbf{r}_{ij}\cdot\frac{\partial\phi(\mathbf{r}_{ij})}{\partial\mathbf{r}_{ij}}. \tag{6}$$

An alternative method of calculating the Grüneisen parameter would be to fit a number of Monte Carlo isotherms to a Grüneisen-type equation of state. This has been done by Jacobs[11] using the high-temperature gaseous isotherms of Fickett and Wood.[12] However, this procedure is equivalent to taking a numerical derivative of the pressure and is inherently less accurate than the exact procedure described here.

Harmonic Approximation

In the harmonic approximation, one may define individual normal-mode Grüneisen parameters[1] by means of the equation

$$\gamma_\alpha \equiv -\left(\frac{d\ln\nu_\alpha}{d\ln V}\right), \tag{7}$$

---

[8] M. Ross, Phys. Rev. **171**, 777 (1968).

[9] V. P. Kopyshev, Soviet Phys.—Doklady **10**, 338 (1965).

[10] N. Bohr, Kgl. Danske Videnskab. Selskab, Mat.-Fys. Medd. **18**, No. 8 (1948); K. S. Pitzer, *Quantum Chemistry* (Prentice-Hall, Inc., Englewood Cliffs, N. J. 1954), p. 202.

[11] S. J. Jacobs, in *Proceedings of the Twelfth Symposium on Combustion* (The Combustion Institute, Pittsburgh, 1969), p. 501.

[12] W. Fickett and W. W. Wood, Phys. Fluids **1**, 204 (1960).

TABLE I. Calculated Grüneisen parameters.

V (cc/mole)	M. C.	$(\mathrm{LJD})_{\mathrm{full}}$	$(\mathrm{LJD})_{\mathrm{AH}}$	$(\mathrm{LJD})_{\mathrm{HO}}$	LD	P (0°K) (kbar)
24.19	2.70(±0.1)	2.63	2.66	2.95	2.89	
22.73	2.42	2.53	2.55	2.75	2.69	
19.53	2.25	2.32	2.33	2.40	2.37	
17.97	2.15	2.22	2.22	2.27	2.24	
			Pressure at 65°K (kbar)[a]			
24.19	0.07(±0.05)	0.03	0.04	0.23	0.18	−1.75
22.73	1.29	1.28	1.29	1.42	1.38	−0.54
19.53	8.08	8.05	8.06	8.11	8.08	6.12
17.97	15.50	15.46	15.47	15.51	15.48	13.46

[a] Monte Carlo pressures for this potential are reported in Ref. 5.

where ν_α is the normal-mode frequency of the αth normal mode and γ_α is the corresponding Grüneisen parameter. For temperatures high enough to permit the assumption of equipartition of energy among the modes, the Grüneisen parameter for the whole crystal will be the average of the individual γ_α's for all the normal modes,

$$\gamma_{\mathrm{LD}} = \frac{1}{3(N-1)} \sum_\alpha \gamma_\alpha , \tag{8}$$

where N is the number of particles in the crystal.

We have calculated γ_{LD} for a 108-particle lattice with periodic boundary conditions in the following way: At a given volume, we use the exponential-6 potential of Eq. (3) to calculate the coupling parameters for the first four complete shells of neighbors. This method of determining the coupling parameters is commonly referred to as the quasiharmonic approximation. The 3×3 dynamical matrix[5] is calculated and diagonalized for 107 wave vectors in the first Brillouin zone of the lattice. The 321 eigenvalues are the squares of the normal-mode frequencies for the lattice. Finally, we calculate the derivatives of the normal-mode frequencies given in Eq. (7) by repeating the process for several closely spaced volumes and taking the appropriate differences. By performing the average indicated in Eq. (8), we obtain γ_{LD}. Values of γ_{LD} are given in Table I and Fig. 1.

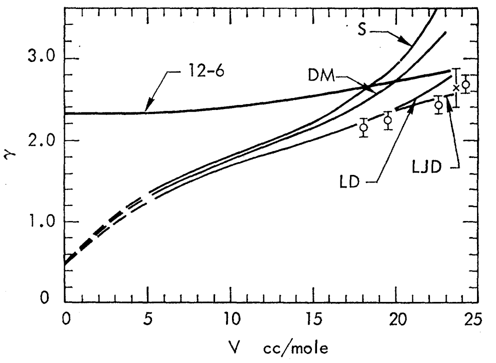

FIG. 1. Comparison of γ as a function of volume at 65°K calculated by means of the Slater formula (S), lattice dynamics (LD), and the LJD cell model (LJD). The circles are the results of Monte Carlo calculations and the X is the value measured by Peterson *et al.* (Ref. 15). The bars indicate the experimental or computational error. The curve labeled 12-6 was calculated by means of the LJD cell model using the Lennard-Jones 12-6 interatomic potential.

In order to make a comparison with the Monte Carlo pressure, the pressure has been calculated for the classical harmonic approximation using Eq. (2),

$$P(65°\mathrm{K}) = P(0) + \gamma(\Delta E/V)_V \quad \text{and} \quad (\Delta E)_V = 3R\times 65 ,$$

which is exact in this case.

Using the pair potential of Eq. (3), we can write the total energy of the lattice at 0°K as

$$E = \tfrac{1}{2} N \sum_j \phi(r_{1j}) , \tag{9}$$

where the sum is over all the neighbors of atom 1. The pressure at 0°K is

$$P(0°) = -\left(\frac{\partial E}{\partial V}\right)_{T=0°\mathrm{K}} . \tag{10}$$

The results for $P(65°\mathrm{K})$ are shown in Table I.

The Monte Carlo calculation and the lattice dynamics calculation have both been made for 108 particles with periodic boundary conditions. Both are exact calculations and differ only in that the Monte Carlo calculations make use of the full interatomic potential, whereas the lattice dynamics method uses only the harmonic form of the interatomic potential so that by comparing the two results, one may determine the importance of the anharmonic contributions to the Grüneisen parameter and to the pressure.

In addition to calculating γ_{LD} and P for comparison with other calculations, we have investigated two other problems by means of the lattice dynamics calculations. First, we have considered the number dependence of γ. Since all the calculations listed in Table I are for 108-particle systems (with periodic boundaries), one may ask how well such a small system represents a real crystal with 10^{23} particles. This question is most easily answered by means of the lattice dynamics calculation because to increase N, one simply considers wave vectors more closely spaced in the Brillouin zone. We calculated values of γ_{LD} for systems of 108, 256, 500, and 864 particles at each of the volumes given in Table I. These values indicate that γ_{LD} is linear in $1/N$ with a slope of -0.007 and the value for $\gamma_{\mathrm{LD}}(N=\infty)$ agrees with $\gamma_{\mathrm{LD}}(N=108)$ to three significant digits. This result leads us to believe that 108 atoms in a Monte Carlo calculation will also be an adequate representation for determining the properties of the infinite system. Finally, we have investigated the distribution of the γ_α's about the average. These results are given in Table II. At each volume, we round off the γ_α's to two significant digits and tabulate the number of γ_α's having each value. The individual parameters lie in a fairly narrow range near the average γ, and they tend to converge on the average value at the high densities. At the lower densities, the γ_α's for the transverse modes are smaller than those for the longitudinal modes, so that the distribution exhibits two separate maxima. This may be represented by

$$\gamma=\tfrac{1}{3}\gamma_l+\tfrac{2}{3}\gamma_t;\quad \gamma_l\neq\gamma_t \text{ at lower densities},$$
$$\gamma_l=\gamma_t \text{ at high densities}.$$

Here, γ_l and γ_t are, respectively, the average longitudinal and transverse parameters.

Since the anharmonic terms will be more important at the lower densities and the harmonic approximation will become more valid at the higher densities, this suggests that $\gamma_l\neq\gamma_t$ when anharmonic terms are nonnegligible and $\gamma_l=\gamma_t$ when the anharmonic terms are negligible.

TABLE II. Distribution of normal mode γ's at four volumes.

γ_α \ V (cc/mole)	17.97	19.52	22.73	24.19
2.1	28			
2.2	174	28		
2.3	93	138		
2.4	26	72	12	
2.5		77	52	12
2.6		6	78	16
2.7			60	60
2.8			39	78
2.9			62	36
3.0			12	36
3.1			6	51
3.2				14
3.3				12
3.4				6

Lennard-Jones-Devonshire (LJD) Cell Model

The LJD model is a one-particle model of the solid. Each atom moves independently of its neighbors in a field obtained by summing the interatomic pair potential over all the stationary neighbors and then taking a spherical average of this potential. The spherical average of the potential field was then taken over the first four shells of nearest neighbors using the pair potential of Eq. (3). The Grüneisen parameter was calculated by evaluating $V/R(\partial P/\partial T)_V$ and C_V/R and using Eq. (1). The calculations are listed in Table I as $(\text{LJD})_{\text{full}}$ and are shown in Fig. 1. Since most calculations of the Grüneisen parameter make use of a harmonic model, calculations were carried out using the harmonic approximation to the LJD cell potential listed as $(\text{LJD})_{\text{HO}}$. Calculations were also made using the next higher approximation, which is the harmonic term, plus first anharmonic term which in the spherical approximation is $0(r^4)$. The latter is listed as $(\text{LJD})_{\text{AH}}$ in Table I.

Slater and Dugdale-MacDonald

Two widely used methods of calculating the Grüneisen parameter are those of Slater,

$$\gamma_{\text{SL}}=-\tfrac{1}{2}V\frac{\partial^2P/\partial V^2}{\partial P/\partial V}-\tfrac{2}{3},\tag{11}$$

and Dugdale and MacDonald,

$$\gamma_{\text{DM}}=-\tfrac{1}{2}V\frac{\partial^2(PV^{2/3})/\partial V^2}{\partial(PV^{2/3})/\partial V}-\tfrac{1}{3}.\tag{12}$$

Using Eq. (10) in Eqs. (11) and (12) allows us to calculate the Slater and Dugdale-MacDonald γ's for this pair potential. These results are shown in Fig. 1.

III. DISCUSSION

The results in Table I and Fig. 1 show clearly that for the classical solid the LJD model using the full potential or the anharmonic potential is in good agreement with the results of the Monte Carlo calculations. The LJD model using only the harmonic potential is in good agreement with the results of the lattice dynamics. Both lattice dynamics and LJD harmonic models are not in agreement with Monte Carlo results at low density, but are in agreement at the higher densities where the harmonic approximation presumably becomes valid. This convergence occurs at about 18 cc/mole. These results show that in the case of rare-gas crystals at classical temperatures and relatively low pressures, the anharmonic corrections are not negligible and should be included if an accurate intermolecular force is to be derived from the measured properties of the crystal by lattice dynamics calculations. A comparison of the Dugdale-MacDonald equation to that of Slater shows the Dugdale-MacDonald equation to be superior, but both are in poor agreement with the lattice dynamics calculations except at very high compressions where all the results converge.

It is noteworthy that our detailed calculations support the assumptions made by Pastine[13] in the derivation of an approximate formula for γ_{LD}. Noting that the inadequacy of the Slater formula is due primarily to the fact that it treats γ_l and γ_t as if they had the same volume dependence, Pastine treated them separately by assuming that γ_l and γ_t could be closely approximated by the longitudinal and transverse γ's for a single phonon propagation direction, the principal axis of the crystal. The fact that we observe that the individual longitudinal and transverse γ's lie in a fairly narrow range about their respective averages lends credence to Pastine's assumption. Moreover, for $V=24.19$ cc/mole (the most sensitive test of these assumptions among our calculations) we have calculated the average γ_l and γ_t for phonons traveling along the principal axis of the crystal to be 3.16 and 2.80, respectively. The weighted average $\gamma_{l/3}+2\gamma_{t/3}$ is 2.92 which is indeed very close to $\gamma_{\text{LD}}=2.89$ for this volume.

Up to this point, we have refrained from a comparison of our results with those of experiment in order to em-

---

[13] D. J. Pastine, Phys. Rev. **138**, A767 (1965).

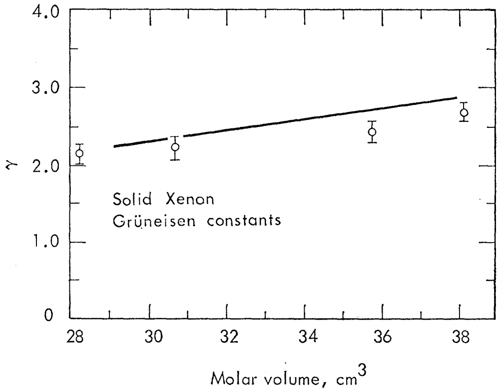

FIG. 2. The Monte Carlo γ's, scaled to represent xenon γ's are compared to an experimental curve (Ref. 14).

phasize the importance of comparing models for an exactly known potential rather than having to infer a potential from experiment. However, the usefulness of this work will be extended if it can be shown to be directly applicable to the actual volume dependence of real systems. To our knowledge the most extensive measurements of γ as a function of volume are those of Packard and Swenson[14] for xenon. These results are for temperatures above the Debye temperature and thereby allow a direct comparison with our classical calculations. The calculations of γ in Table I have been for a potential simulating argon, and the results may be scaled to one simulating xenon by the use of the corresponding states scaling law.[7] We have used the ratios of the triple-point volumes to obtain the corresponding xenon volumes and the ratio of the triple-point temperatures to obtain a xenon isotherm temperature which becomes 125.15°K and is above the Debye temperature. Since γ is a dimensionless quantity, it does not scale. The results of γ as a function of volume compared to experiments for xenon are shown in Fig. 2. The agreement is within the experimental (±0.1) and computational error, and it is significant to note that both curves have the same variation with respect to volume. An experimental measurement of Peterson *et al.*[15] for argon shown in Fig. 1 is also in good agreement with calculations.

TABLE III. Calculations of anharmonic corrections to the lattice dynamics γ.

T (°K)	V (cc/mole)	γ_{LD}	$\Delta\gamma$	γ_{AH}
4	22.557	2.446	−0.017	2.429
10	22.563	2.538	−0.043	2.495
20	22.645	2.614	−0.079	2.535
30	22.804	2.659	−0.117	2.542
40	23.026	2.698	−0.159	2.539
50	23.296	2.740	−0.206	2.534
60	23.611	2.786	−0.260	2.526
70	23.983	2.841	−0.324	2.517
80	24.435	2.910	−0.401	2.509

Peterson *et al.*[15] have also measured γ as a function of temperature at zero pressure. These results are shown in Fig. 3. The experiments show a distinct maximum, with the γ increasing with temperature at low temperatures and decreasing with increasing temperature at high temperatures. We have attempted to reproduce this curve by using the following method: Let

$$\begin{aligned}\gamma_{\mathrm{CAL}}(V,T)&=\gamma_{\mathrm{LD}}(V,T)+\Delta\gamma(V,T)_{\mathrm{LJD}},\\ \Delta\gamma(V,T)_{\mathrm{LJD}}&=\gamma(V,T)_{\mathrm{full}}-\gamma(V,T)_{\mathrm{HO}},\end{aligned}\tag{13}$$

and

$$\gamma_{\mathrm{LD}}(V,T)=\sum_{\alpha=1}^{3(N-1)}\gamma_\alpha\left[h\nu_\alpha/(e^{h\nu_\alpha/kT}-1)\right]\Big/\sum_{\alpha=1}^{3(N-1)}h\nu_\alpha/(e^{h\nu_\alpha/kT}-1).\tag{14}$$

These calculations were made at the temperatures and volumes along the $P=0$ equilibrium curve, as measured by Peterson *et al.* In other words, the calculated Grüneisen parameter γ_{calc} will be equal to the quantum-mechanical lattice dynamics γ plus an anharmonic correction $\Delta\gamma(V,T)$ based on the LJD model in which the anharmonic contributions are taken to be the difference between an LJD calculation made with the full potential and one made in the harmonic approximation. This approximation is equivalent to expressing the free energy as

$$F(V,T)=F_{\mathrm{LD}}(V,T)+\Delta F(V,T)_{\mathrm{LJD}},$$

where

$$\Delta F(V,T)_{\mathrm{LJD}}=F(V,T)_{\mathrm{full}}-F(V,T)_{\mathrm{HO}}.\tag{15}$$

The LJD model is a classical model and cannot be used at low temperatures where quantum effects are important. However, for argon at low temperatures where quantum effects are important, the anharmonic corrections are small, and only become important at the higher temperatures where quantum effects become negligible. Consequently, the approximations made in Eq. (13) should be adequate. A more correct procedure would be to calculate $\Delta\gamma$ using a quantum cell model, or a model similar to Zucker's[16] which calculates thermal properties for the quantum-mechanical anharmonic oscillator. The results of using Eq. (13) are shown in Fig. 3 and Table III, and the curve with the anharmonic corrections display the same qualitative trend as the experimental results while the curve without the corrections continues to rise. The agreement between calculations and experiment (±0.1) must also be considered good. The largest qualitative disagreement occurs at the highest temperatures where the experimental values drop off more steeply than the calculations. However, it is in this region that the experiments have their largest uncertainty which the authors report to be ±10%. Un-

---

[14] J. R. Packard and C. A. Swenson, J. Phys. Chem. Solids **24**, 1405 (1963).

[15] O. G. Peterson, D. N. Batchelder, and R. O. Simmons, Phys. Rev. **150**, 703 (1966).

[16] I. J. Zucker, Phil. Mag. **3**, 987 (1958).

fortunately, the magnitude of the error leads to the possibility that this experimental decrease in γ may be spurious. Our calculations indicate it to be at least qualitatively correct. A similar behavior in the high-temperature variation of Grüneisen parameter was obtained by Feldman *et al.*[17] using a semiempirical model. The change in γ with temperature along the equilibrium curve arises from two contributions. First, the temperature increases and second, the crystal expands. In order to separate these two effects, we have used Eqs. (13) and (14) to calculate γ as a function of temperature but at a fixed volume, $V=24.19$°K. These results are in Fig. 3. They show that the increase in γ at low temperatures is due primarily, though not exclusively, to the thermal expansion. At higher temperatures and at constant volume, γ is decreasing more rapidly with increasing temperature than is the curve at the equilibrium volumes. At the high temperatures, the general trend is for γ to increase with expansion (see Fig. 1). Consequently, there is some cancellation, with the anharmonic terms dominating. Thus, the high-temperature decrease results primarily from the increasingly important contribution of the anharmonic terms. The quantity $\Delta\gamma$ is linear with T at low temperatures, in agreement with theoretical predictions.[3]

From the theoretical considerations and the analysis of high-energy atomic scattering data, the exponential form of the rare-gas potential is known to be a better representation of the repulsive interaction between closed atoms than is the inverse power potential. Nevertheless, because of its mathematical simplicity and its apparent adequacy near the minimum of the interaction curve, the Lennard-Jones 12-6 potential is the most widely used rare-gas intermolecular potential. In the case of a 12-6 potential, γ of 2.89 was calculated at 65°K and $V=24.19$ cc/mole using the LJD model with $\epsilon/k=119.76$°K and $r^*=3.822$ Å. However, the γ calculated varies but slowly with volume, and at highest compressions where only the repulsive forces are important becomes $\gamma=[\frac{1}{6}n+\frac{1}{3}]=2.33$. From an analysis of a considerable amount of shock data, it is known that in general γ varies more rapidly with compression and consequently infers that the inverse 12 power potential is inappropriate for highly compressed materials. This would appear to be verified by a γ curve for this potential shown in Fig. 1 wherein it is seen that calculated values for the 12-6 potential vary much more slowly than experiment and, of course, approach an incorrect limiting value for γ at infinite compressions.

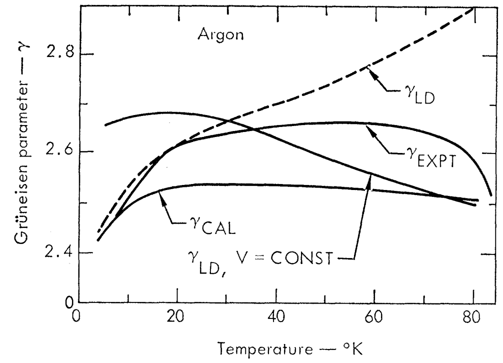

FIG. 3. Comparison of calculated γ's with those measured (Ref. 15) at $P=1$ atm. The curve labeled γ_{LD} is a quantum-mechanical γ obtained from lattice dynamics at the same temperatures and volumes as the experiments using Eq. (15). A similar calculation at constant volume is γ_{LD}, $V=24.19$ cc/mole. The curve labeled γ_{cal} is the lattice dynamical γ, γ_{LD}, which has been corrected for anharmonic effects using Eq. (14).

The question necessarily arises as to whether on the basis of this work any generalizations can be made as to the functional variation of γ with volume. It would appear that for closed-shell systems, such as rare gases and ionic materials in which the equation of state at high compressions are determined primarily by the closed shell repulsive forces, the linear approximation $\gamma=CV+\gamma_0$, in which γ_0 has the correct limiting value at $V=0$, will be appropriate. C is a constant and could be determined from a known γ at some V. Empirical relations of the form $\gamma=CV^n$ have been used. However, we wish to point out that these relations neglect a consideration of the limiting form of γ at $V=0$ and must lead to incorrect results at very high compression. We do not believe that the present work can be directly extended to metals because of the sensitivity of γ to the exact form of the potential; however, the arguments concerning the importance of the correct limiting value of γ are valid for all systems of matter and should be taken into account, particularly in geophysical applications where extreme compressions are common.

ACKNOWLEDGMENT

One of us (M. R.) wishes to thank Dr. B. Alder for many useful conversations during the preliminary stages of this work.

---

[17] C. Feldman, J. L. Feldman, G. K. Horton, and M. L. Klein, Proc. Phys. Soc. (London) **90**, 1182 (1967).