# Low-Temperature Anharmonicity and the Debye-Waller Factor\*

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Low-temperature anharmonicity plays an important role in ferroelectrics, high-field superconductors, light molecular solids, and other classes of materials of current interest. The Debye-Waller factor f, which in the harmonic approximation is a measure of the mean-square atomic displacement, is a useful gauge in the degree of low-temperature anharmonicity. The f factor and its temperature dependence are discussed for several simple models in which the potentials are such that low-temperature atomic displacements are large enough to sample deviations from harmonic potential shapes. The / factor is factorable in the classical temperature regime into harmonic and anharmonic terms, and also at low temperatures in certain limiting cases. Factorization facilitates the analysis of experimental data to yield a gauge of low-temperature anharmonicity.

#### I. INTRODUCTION

HE basis of the modern theory of lattice dynamics is the assumption that a harmonic approximation is asymptotically correct at low temperatures.<sup>1-3</sup> Although the harmonic approximation seems to be quite satisfactory for most solids at low temperatures, it has been known for some time that there are certain classes of materials for which it is rather poor.

One such class is composed of the light van der Waals solids such as Ne, D<sub>2</sub>, H<sub>2</sub> and especially He<sup>4</sup> and He<sup>3,4,5</sup> In these crystals, the zero-point kinetic energy is significant in comparison to the cohesive energy, causing the crystals to have, at moderate pressures, appreciably greater interatomic distances than those corresponding to the superposition of nearest-neighbor potential minima. The effect of this expansion is to produce a relatively large and field-free volume within which each molecule moves, for the entire temperature range of existence of the crystal, down to T=0. The boundaries of the atomic volume are effectively established by the repulsive cores of the first-neighbor shell, and these potentials rise quite steeply. The combination of these effects tends to distort the potential from a quasiharmonic shape toward that of a square well. In the extreme cases of He<sup>3</sup> and He<sup>4</sup>, the potential is higher in the center than near the boundaries.<sup>5</sup> Such potential curves have been described by Lennard-Jones and Devonshire<sup>6</sup> for dense van der Waals gases, and are illustrated in Fig. 1.

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<sup>a</sup> G. L. Pollack, Rev. Mod. Phys. 36, 748 (1964).
<sup>b</sup> C. Domb and J. S. Dugdale, in Progress in Low Temperature Physics, edited by C. J. Gorter (North-Holland Publishing Co., Amsterdam, 1957), Vol. II.
<sup>b</sup> I. E. Lennard-Iones and A. F. Devonshire, Proc. Roy. Soc.

<sup>6</sup> J. E. Lennard-Jones and A. F. Devonshire, Proc. Roy. Soc. (London) A163, 53 (1937).

such distortions from harmonic potentials is the clathrates, or inclusion compounds, such as hydroquinone.7 These compounds have crystal structures which contain regular cavities capable of containing single isolated foreign atoms. When the foreign atom is a small rare-gas atom, it is effectively held loosely in a small cage. The potential well in which it is held is rather similar in shape to that of the rare-gas solids, and may have minima near the walls of the cage due to van der Waals attractive forces.

Another well-known class of substances exhibiting

Ferroelectrics and antiferroelectrics fall into several groups,<sup>8,9</sup> and in each type, ferroelectricity appears to arise from fundamental anharmonicities in the potentials of certain of the ions near their centers of symmetry. In the displacive ferroelectrics such as BaTiO<sub>3</sub>, the Ti ions occupy regions appreciably larger than their ionic size, so that they are loosely held in potentials that are flattened in their central regions. The central region of low or negative force constants, together with the Lorentz correction to the dipole moment, accounts for the essential features of the ferroelectric behavior.<sup>10</sup> Theories of ferroelectricity in order-disorder ferroelectrics such as KNO3 are based



FIG. 1. Effective potentials for dense van der Waals gases, for several average densities, after Lennard-Jones and Devonshire (Ref. 6).

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<sup>&</sup>lt;sup>1</sup> R. E. Peierls, *Quantum Theory of Solids* (Oxford University Press, New York, 1955).

upon similar distortions of the atomic potentials.<sup>11,12</sup> In the hydrogen-bonded ferroelectrics, such as potassium dihydrogen phosphate, the hydrogen ions may occupy one of two possible minimum potential-energy sites near PO<sub>4</sub> groups.<sup>13,14</sup>

Numerous studies in recent years indicate that there are several additions to be made to the list of materials exhibiting low-temperature anharmonicity. These include small ionic impurities in ionic crystals, some highfield superconductors, small metal ions in metallic solution, and most recently, certain pure ionic compounds.

Small ionic impurities such as Li<sup>+</sup>, OH<sup>-</sup>, and CN<sup>-</sup> in ionic crystals of KCl and KBr are situated in potentials having several equivalent minima,<sup>15-20</sup> and move among these minima relatively freely at quite low temperatures. Among the properties indicating such anharmonicities are heat capacity, thermal conductivity, infrared absorption, and elastic constants. It appears that the anharmonicity is quite directly the result of the reduced sizes of the impurity ions, together with the normal electrostatic and repulsive-core contributions to the potentials.

The  $\beta$ -tungsten structure compounds Nb<sub>3</sub>Sn, Nb<sub>3</sub>Al, Nb<sub>3</sub>Ga, V<sub>3</sub>Si, and V<sub>3</sub>Ga are all superconductors with transition temperatures above 14°K, and all exhibit elastic softening on cooling.<sup>21,22</sup> The elastic moduli of certain shear waves fall nearly to zero in the superconducting state, this softening being apparently related to the occurrence of high-temperature superconductivity. Recently a study of the Mössbauer effect of Sn<sup>119</sup> in Nb<sub>3</sub>Sn<sup>23</sup> has shown that the low-temperature behavior of the Debye-Waller factor (f factor) deviates quite markedly from that of harmonically bound atoms and the observed temperature dependence can be ininterpreted to indicate that the Sn ions move in potential wells which are markedly anharmonic in their central regions.24-26

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  <sup>19</sup> C. K. Chau, M. V. Klein, and B. Wedding, Phys. Rev. Letters 17, 521 (1966).
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- <sup>23</sup> J. S. Shier and R. D. Taylor, Solid State Commun. 5, 147 (1967).

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 <sup>25</sup> W. A. Steyert and P. P. Craig, Phys. Letters 2, 165 (1962). The observation that the *f* factor for a square-well potential is independent of temperature (actually, it is exactly constant only

Indications of low-temperature anharmonicity can be adduced from Mössbauer studies of Sn<sup>119</sup> in the binary metallic compounds SnAs, SnSb, SnTe, and SnPt.<sup>27</sup> Very recently, definite evidence of low-temperature anharmonicity has been found for Fe<sup>57</sup> in the ionic compound FeCl<sub>2</sub>.28

The temperature dependence of the *f* factor can provide a relatively direct indication of low-temperature anharmonicity. The applicability of the f factor as a quantitative gauge in such studies has been advanced by the general theory of Housley and Hess,<sup>24</sup> who have derived the limiting conditions on the temperature dependence of the f factor for harmonic interatomic forces, independent of the frequency spectrum of the solid. The present paper explores the influence of lowtemperature anharmonicity on the temperature dependence of the Mössbauer fraction, and describes how the observed temperature dependence of f may be analyzed to obtain some information on the detailed shapes of the interatomic potentials.

#### **II. CALCULATION OF DEBYE-WALLER FACTORS:** GENERAL DESCRIPTION

The Debye-Waller factor f is a particularly sensitive gauge of anharmonicity, since it is directly related to the mean-square displacement of the resonant atom. The well-known expression<sup>29,30</sup> for f, which is exact for harmonic systems, is

$$f = \exp\left(-k^2 \langle x^2 \rangle\right), \qquad (1)$$

where k is the wave number of the  $\gamma$  ray and  $\langle x^2 \rangle$  is the thermal average displacement of the radiating atom. Equation (1) is a good approximation for atomic potentials in which there is a considerable but physically reasonable degree of cubic and quartic "high-temperature anharmonicity".<sup>31,32</sup> The cubic and quartic terms are usually adequate for semiquantitative theories of anharmonic effects such as thermal expansion and specific heat at high temperatures. For materials with flattened wells, however, a power-series expansion is not a useful representation of the potential because, even at the lowest temperatures, the displacement of

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<sup>&</sup>lt;sup>11</sup> S. Sawada, S. Nomura, and Y. Asao, J. Phys. Soc. Japan 16, 2486 (1961).

 <sup>&</sup>lt;sup>12</sup> A. Chen and F. Chernow, Phys. Rev. 154, 493 (1967).
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 <sup>14</sup> R. Blinc and S. Svetina, Phys. Rev. 147, 430 (1966).

in the classical approximation) was made by Steyert and Craig, in an attempt to explain the anomalous temperature dependence of the f of Fe<sup>57</sup> in In. Although their experimental results now appear questionable (see Ref. 26), their original remark concerning the influence on the temperature dependence of f by a flattened

 <sup>&</sup>lt;sup>26</sup> P. A. Flinn, V. Gonser, R. W. Grant, and R. M. Housley, Phys. Rev. **157**, 538 (1967).
 <sup>27</sup> V. A. Bryukhanov, N. N. Delyagin, R. N. Kuz'min, and V. S. Shpinel, Zh. Eksperim. i Teor. Fiz. **46**, 1966 (1964) [English transl.: Soviet Phys.—JETP **19**, 1344 (1964)].
 <sup>28</sup> D. P. Johnson and J. G. Dash, Bull. Am. Phys. Soc. **12**, 378 (1967)

the atom extends over nonharmonic regions of the interatomic potential.

An alternative approach is to emphasize the independent-particle aspects of the problem, calculating the f factors for individual atoms in individual anharmonic potential wells. In ignoring the collective aspects of the atomic motions, this procedure is likely to produce inaccuracies similar to those of the Einstein model of harmonic solids. As is well known, the Einstein model is inadequate to describe low-temperature heat capacity, because the latter is determined by the low-frequency phonons with energy comparable to or less than kT. The f factor for typical solids, on the other hand, is fixed mainly by the higher-frequency modes. (The mean-square zero-point displacement is proportional to the minus first moment of the phonon spectrum.) Therefore, an independent-particle (Einstein) model calculation can give a reasonable first approximation to the Debye-Waller factor but not the heat capacity. The temperature derivative of the f factor, though, will be inaccurate for the same reason that the heat capacity is.

In addition, we find it possible to improve the singleparticle approximation by incorporating some features of the collective motions, as is described in Sec. IV. For most of the materials under discussion, the anharmonicity is limited to the interactions between certain atoms and their immediate neighbors, while the remaining interactions in the crystal are essentially harmonic. This is the situation, for example, in the case of dilute ionic impurities, for rare-gas atoms in clathrates, and probably also in FeCl<sub>2</sub>. In favorable cases, the fact that the long-range (and low-frequency) interactions are basically harmonic will allow us to superimpose these collective motions on the highly anharmonic independent-particle motions, and to treat the combination in a straightforward calculation. We find that the resulting Debye-Waller factor is a product of separate factors due to the harmonic collective and anharmonic independent-particle motions, and in this form is useful for comparisons with experimental observations.

The general expression for the f factor is, for stationary states of the crystal  $|n_{\alpha}\rangle$ , nuclear coordinate  $\mathbf{r}_{0}$  of the active atom, and radiation wave vector  $\mathbf{k}$ ,

$$f = \sum_{\alpha} w_{\alpha} |\langle n_{\alpha} | e^{i\mathbf{k} \cdot \mathbf{r}_{0}} | n_{\alpha} \rangle|^{2}, \qquad (2)$$

where  $w_{\alpha}$  is the Boltzmann weighting factor for the  $\alpha$  state.<sup>30</sup> Lipkin has shown that if  $|n_{\alpha}\rangle$  is not really a stationary state but, as is always the case in practical calculations, relaxes rapidly compared to the  $\gamma$ -ray lifetime, then the matrix element should be squared *after* the thermal averaging. Therefore we may write

$$\sqrt{f} = \frac{\operatorname{Tr}(e^{-\beta H}e^{i\mathbf{k}\cdot\mathbf{r}_{0}})}{\operatorname{Tr}(e^{-\beta H})},$$
(3)

where  $\beta = 1/kT$ , and

$$H = \sum_{j} \frac{p_{j}^{2}}{2m_{j}} + V(\mathbf{r}_{1}, \mathbf{r}_{2}, \cdots, \mathbf{r}_{0}, \cdots, \mathbf{r}_{N})$$

is the Hamiltonian of the entire crystal. For the region of classical temperatures, the trace becomes an integral over all particle coordinates and momenta,

$$\sqrt{f} = \int e^{-\beta H} e^{i\mathbf{k}\cdot\mathbf{r}_{0}} \prod_{j} d^{3}r_{j}d^{3}p_{j} / \int e^{-\beta H} \prod_{j} d^{3}r_{j}d^{3}p_{j}$$

$$= \int \exp\left[-\beta V(\mathbf{r}_{1}, \mathbf{r}_{2}, \cdots, \mathbf{r}_{0}, \cdots, \mathbf{r}_{N}) + i\mathbf{k}\cdot\mathbf{r}_{0}\right] \prod_{j} d^{3}r_{j} / \int \exp\left[-\beta V(\mathbf{r}_{1}, \mathbf{r}_{2}, \cdots, \mathbf{r}_{0}, \cdots, \mathbf{r}_{N})\right] \prod_{j} d^{3}r_{j}. \quad (4)$$

In the simple case of independent particles in individual potentials,

$$V(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_0, \cdots, \mathbf{r}_N) = \sum_{j} V_j(\mathbf{r}_j),$$

so that we obtain, after cancellation,

$$\sqrt{f} = \int e^{-\beta V_0(\mathbf{r}_0)} e^{i\mathbf{k}\cdot\mathbf{r}_0} d^3 r_0 \bigg/ \int e^{-\beta V_0(\mathbf{r}_0)} d^3 r_0.$$
 (5)

Equation (5) is a classical independent-particle expression, valid for the region in which the separations between the independent-particle states are much smaller than kT.

In the limit T=0, the Debye-Waller factor is given directly by the matrix element for the ground state of the crystal  $|0\rangle$ :

$$f(0) = |\langle 0 | e^{i\mathbf{k} \cdot \mathbf{r}_0} | 0 \rangle|^2, \qquad (6)$$

and therefore requires that the Schrödinger equation be solved for the particular potential of interest. It is important to note that it is only for harmonic potentials that Eqs. (5) and (6) are equivalent to Eq. (1). The application of Eq. (1) to highly anharmonic systems, as has been done by Schmidt<sup>33</sup> may lead to considerable error, as we show in a later section.

In the following section we will apply Eqs. (5) and (6) to particular well shapes, studying the high-temperature and T=0 behavior of f in the independent-particle approximation.

<sup>&</sup>lt;sup>33</sup> H. Schmidt, Phys. Rev. 156, 552 (1967).

## III. LOW-TEMPERATURE ANHARMONICITY: INDEPENDENT-PARTICLE WELLS

One of the earliest papers on recoilless resonance fluorescence<sup>34</sup> is a description of the radiation from a one-dimensional ideal Maxwellian gas in a rigid enclosure. A classical calculation leads to the result that the radiation contains a sharp non-Doppler broadened line of relative intensity

$$\frac{\sin^2(\pi d/\lambda)}{(\pi d/\lambda)^2},\tag{7}$$

where d is the dimension of the well. The same result can be shown to hold for any velocity distribution. There are two features of this result that are markedly different from the Debye-Waller factor of harmonically bound atoms: For the square well the fraction is independent of the temperature, and it has a spectrum of zeros at the values  $d=n\lambda$ ,  $n=1, 2, \cdots$ . The high-temperature solution obtained by using Eq. (1), which is not appropriate for this problem, is  $f = \exp(-\pi^2 d^2/3\lambda^2)$ . Although this result approaches the correct expression at small d, it deviates by considerable amounts at moderate d and shows no interference. The zeros are not physically important features of the Mössbauer



FIG. 2. Amplitude of the Mössbauer fraction for a spherical cavity, for high temperatures and at T=0.

34 R. H. Dicke, Phys. Rev. 89, 472 (1953).

effect, however, since they are essentially undetectable in practical cases. For the above one-dimensional example, the peak intensity in the first subsidiary maximum is only about 10% of the central peak. In the three-dimensional wells and in those with softer walls the subsidiary peaks are very much weaker, as will be seen. The temperature independence is extreme in this simple example, for a certain variation with temperature will be seen to arise when the walls are softened. Furthermore, even in the present example, it is only in the classical high-temperature limit that f is independent of T. These features are illustrated in the following example, a three-dimensional infinitely deep square well of radius  $R_0$ . At high temperatures, we obtain by Eq. (5)

$$\sqrt{f} = \frac{3}{(kR_0)^2} \left( \frac{\sin kR_0}{kR_0} - \cos kR_0 \right),$$

for

$$V(\mathbf{r}) = 0, \quad 0 < r < R_0$$

$$V(\mathbf{r}) = \infty, \quad r > R_0.$$
(8)

The f factor is independent of T in this classical limit. The importance of the interference phenomenon is sharply reduced below its effect in the one-dimensional case, since the magnitude of the secondary peak is now only about 0.01. For low temperatures, f is calculated according to Eq. (6). The ground-state wave function for the infinite square well is

$$|0\rangle \propto \sin(\pi r/R_0)/r$$
, (9)

which yields

$$\sqrt{f} = \frac{1}{2kR_0} \int_{-kR_0}^{kR_0} \frac{\sin x}{x(1+x/2\pi)} dx.$$

This function along with Eq. (8) is plotted in Fig. 2. It again shows interference effects but they are sharply reduced below those for the high-temperature regime.

The interference is further suppressed if the realism of the single-particle well is enhanced by softening its walls. A simple shape having the desired characteristics was used by Kincaid and Eyring<sup>35</sup> for the molecular potential in a liquid. As illustrated in Fig. 3, the potential can be written in the form

$$V(r) = 0, \qquad 0 < r < R_0 V(r) = \frac{1}{2}\kappa(r - R_0)^2, \quad r > R_0.$$
(10)



<sup>35</sup> J. G. Kincaid and H. Eyring, J. Chem. Phys. 5, 587 (1937).

A straightforward calculation of Eq. (5) yields

$$\sqrt{f} = \frac{\left[3/(kR_0)^2\right](\sin kR_0/kR_0 - \cos kR_0) + 3(\pi/2\beta\kappa R_0^2)^{1/2}(\sin kR_0/kR_0 + \cos kR_0/\beta\kappa R_0^2)\exp(-k^2/2\beta\kappa)}{1 + 3(\pi/2\beta\kappa R_0^2)^{1/2}(1 + 1/\beta\kappa R_0^2)}.$$
 (11)

Equation (11) reduces to Eq. (8) for  $\kappa \to \infty$  (hard walls). For high temperatures ( $\beta \to 0$ ), Eq. (11) becomes

$$\sqrt{f} = (\cos kR_0)e^{-k^2/2\beta\kappa}.$$
 (12)

The exponential factor is just the high-temperature result for the harmonic oscillator, while the cosine term clearly arises from the flattened central region. The Mössbauer fraction is thus approximately given by the product of harmonic and anharmonic factors. Variation of radius and hardness of the potential well can cause the temperature dependence of f to vary continuously from the square-well limit (no temperature dependence at high temperature) to that of the harmonic lattice, which at high temperatures corresponds to a linear increase in the mean-square displacement.

Although physically reasonable values of  $kR_0$  usually give  $\cos kR_0$  nearly equal to unity, Eq. (11) can, in principle, separate the magnitude of f from its temperature dependence, a feature shared by the models which we study in the following section.

## IV. COUPLED DEGREES OF FREEDOM

An obvious shortcoming of the single-particle models is that the dynamics of all the rest of the lattice is ignored. A first step in the direction of correcting this deficiency is to replace the rest of the lattice by an idealized harmonic system, coupled anharmonically to our single particle. In such a case, if the lattice is described by coordinates  $\mathbf{p}_i$ ,  $\mathbf{r}_i$ , the single particle by  $\mathbf{p}$ ,  $\mathbf{r}$ , and if the single particle interacts with only one of the lattice sites (i=0) with a potential  $V(\mathbf{r}-\mathbf{r}_0)$ , then Eq. (5) gives

$$\sqrt{f} = \frac{\operatorname{Tr}(e^{-\beta H}e^{i\mathbf{k}\cdot\mathbf{r}})}{\operatorname{Tr}(e^{-\beta H})} = \frac{\operatorname{Tr}(e^{-\beta H_0}e^{i\mathbf{k}\cdot\mathbf{r}_0}) \operatorname{Tr}(e^{-\beta V(\rho)}e^{i\mathbf{k}\cdot\rho})}{\operatorname{Tr}(e^{-\beta H_0}) \operatorname{Tr}(e^{-\beta V(\rho)})}, \quad (13)$$

where  $H=H_0+V(\mathbf{r}-\mathbf{r}_0)$ , and  $H_0$  is the harmonic Hamiltonian of the crystal. The relative coordinate  $\mathbf{g}=\mathbf{r}-\mathbf{r}_0$ . Equation (13) is just the product of factors for the lattice and that for the single particle. The former factor corresponds to the usual harmonic term, while the latter factor sets apart the contribution due to the low-temperature anharmonicity.

At low temperatures, quantum effects are important, and the coordinate transformation which yielded Eq. (13) no longer leads to a clean separation into two factors, because of the noncommutative operators. We must use approximate methods, for which the starting points are the limiting cases where either the motion of the particle is fast compared to the important modes of the lattice or vice versa. We can then consider one system to be static while a wave function is established for the other. This is the Born-Oppenheimer approximation of molecular physics. It leads to a zero-order wave function in the form of a simple product, and this can form the basis for a perturbation series.

A very simple model of this type is shown in Fig. 4. The active atom of mass m and coordinate  $\mathbf{r}$  is inside a hard spherical shell of mass M centered at  $\mathbf{R}$  by harmonic springs. The Hamiltonian of this system is

$$H = \frac{P^2}{2M} + \frac{1}{2}\kappa R^2 + \frac{p^2}{2m} + V(\mathbf{r} - \mathbf{R}), \qquad (14)$$

where

$$V(\mathbf{r}-\mathbf{R})=0, \quad r-R < R_0$$
$$V(\mathbf{r}-\mathbf{R})=\infty, \quad r-R > R_0.$$

The integrals of Eq. (13), for the classical temperature regime, may readily be performed by transforming to relative coordinates. The result is

$$\sqrt{f} = \frac{3}{(kR_0)^2} \left[ \frac{\sin kR_0}{kR_0} - \cos kR_0 \right] e^{-k^2/2\beta\kappa}.$$
 (15)

Equation (15) is again the product of two familiar terms, one factor corresponding to the spherical square well and the other to the harmonic oscillator.

The evaluation of the recoilless fraction is more difficult for T=0, where Eq. (6) is appropriate, because one must find the ground-state eigenfunction of the Hamiltonian given by Eq. (14). An analytical form for the wave function can be obtained only approximately, with an accuracy which depends on certain parameters in H. For example, if we assume that the frequency of oscillation of the tennis ball is small compared to that of the particle within it, then we can approximate the wave function by a product of the ground-state harmonic oscillator and square-well wave functions

$$\psi(r,R) \propto e^{-\gamma R^2/2} \frac{\sin\left(\pi \left| \mathbf{r} - \mathbf{R} \right| / R_0\right)}{\left| \mathbf{r} - \mathbf{R} \right|}, \qquad (16)$$

where  $\gamma = (\kappa M/\hbar^2)^{1/2}$ . Using this wave function, we

FIG. 4. An idealized model having harmonic and anharmonic forces which may be solved exactly in certain limiting cases: a BB in a tennis ball.



obtain

$$\sqrt{f} = e^{-k^2/4\gamma} \frac{1}{2kR_0} \int_{-kR_0}^{kR_0} \frac{\sin x}{x(1+x/2\pi)} dx, \qquad (17)$$

which again is the product of terms for the harmonic oscillator and for the spherical square well.

A further improvement in realism is obtained if we adopt a model for the lattice which has many degrees of freedom. That is, we wish to replace the discrete harmonic mode of M in the previous model by a distribution of harmonic modes, while retaining the highly anharmonic character of the single-particle well. When this complication is added the resultant problem can again be solved exactly in the high-temperature region. The model we now envision has our active atom bound by an anharmonic potential  $V(\mathbf{r}-\mathbf{r}_0)$  to a site having coordinates  $(\mathbf{p}_0, \mathbf{r}_0)$  of a harmonic lattice. A mechanical example of such a system is an array of rigid, hollow spheres interconnected by Hookeian springs; one of the spheres confines the extra particle. This model may be appropriate to some of the impurity systems discussed in the Introduction. The Hamiltonian for such systems is

$$H = H_{\text{lattice}} + \frac{p^2}{2m} + V(\mathbf{r} - \mathbf{r}_0).$$
(18)

This Hamiltonian is of the same form as Eq. (14), and therefore the f factor for classical temperatures is factorable, in the sense of Eq. (15).

For low temperatures we must resort to an approximation. Either we consider the extra particle to be light compared to the lattice atoms [corresponding to the result for the simpler model expressed in Eq. (16] or vice versa. In either case we must unmix  $\mathbf{r}$  and  $\mathbf{r}_0$  in  $V(\mathbf{r}-\mathbf{r}_0)$ . For the case of a light active particle one way to do this is to change the variable  $\mathbf{r}$  to  $\mathbf{r}-\mathbf{r}_0$ . Formally, this is accomplished by a unitary transformation,

 $U^{-1}V(\mathbf{r}-\mathbf{r}_0)U=V(\mathbf{r}),$ 

where

$$U = e^{-i\mathbf{r}_0 \cdot \mathbf{p}/\hbar}.$$
 (19)

The transformation can be verified if one recognizes that when  $\mathbf{p} \rightarrow -i\hbar\nabla$ , the expansion of Eq. (19) is the familiar Taylor series. Unfortunately, U does not commute with  $H_{\text{lattice}}$ , because the latter contains  $P_0^2/2M$ . If the commutator  $[U,p_0^2/2M]$  is small compared to the other terms in H, the separation results in a product form for the f factor. The condition for the validity of this conclusion is the same as for Eq. (17), namely that the important lattice frequencies are small compared to those of the single particle.

The other extreme is also interesting. When the characteristic frequencies of the active particle are much smaller than those of the important lattice modes, it is appropriate to build a perturbation method by shifting the lattice coordinates to follow the particle motion rather than the other way around. If the lattice displacements are small compared to the range of V, then

$$V(\mathbf{r}-\mathbf{r}_0)\simeq V(\mathbf{r})-\mathbf{r}_0\cdot\nabla V(\mathbf{r}),\qquad(20)$$

adding a linear term to the potential energy of the lattice, which no longer is a minimum at  $r_j=0$ . The transformation which accomplishes this shift can again be expressed in a form similar to Eq. (19), but now U fails to commute with the particle kinetic energy rather than with that of the lattice, because the translation of coordinates will clearly be proportional to  $\nabla V(\mathbf{r})$ . The transformation operator turns out to be

$$U = \exp\left[i\sum_{l} \frac{\nabla V(r)}{\hbar\omega_{l}^{2}M} \cdot \mathbf{p}_{0}^{l}\right], \qquad (21)$$

where  $\mathbf{p}_0^l$  is the *l*th component of the normal-mode expansion of  $\mathbf{p}_0$ . However, the algebra is more transparent if we use another approach, working with the creation-annihilation operators. The lattice Hamiltonian can then be written<sup>1</sup>

$$H_{\text{lattice}} = \sum_{l} \hbar \omega_l (a_l^{\dagger} a_l + \frac{1}{2}), \qquad (22)$$

where the creation (annihilation) operators  $a_l^{\dagger}(a_l)$  satisfy the usual commutation relations

$$[a_{l},a_{l'}] = \delta_{ll'}. \tag{23}$$

The frequency of the *l*th normal mode in Eq. (22) is  $\omega_{l'}$  and for simplicity, we have restricted ourselves to one direction of polarization  $\hat{e}$ . In terms of the phonon operators, the coordinate and momentum of the center-(zeroth-) particle are

$$\mathbf{r}_{0} = \hat{e} \sum_{l} (\hbar/2MN\omega_{l})^{1/2} (a_{l}^{\dagger} + a_{l}) ,$$
  
$$\mathbf{p}_{0} = i\hat{e} \sum_{l} (M\hbar\omega_{l}/2N)^{1/2} (a_{l}^{\dagger} - a_{l}) \qquad (24)$$
  
$$= \sum_{l} \mathbf{p}_{0}^{l} .$$

The *a*'s will be translated to new operators  $\alpha$ ,

$$\alpha_l = a_l + u_l, \tag{25}$$

by the unitary transformation which translates the coordinates. The  $\alpha$ 's will again satisfy Eq. (23) if the u's commute with the  $\alpha$ 's. Upon expressing the total Hamiltonian [Eq. (22) plus Eq. (20) plus extra-particle kinetic energy] in terms of the  $\alpha$ 's, with the help of Eqs. (24) and (25), we find

$$H = \sum_{l} \hbar \omega_{l} (\alpha_{l}^{\dagger} \alpha_{l} - u_{l} \alpha_{l}^{\dagger} - u_{l}^{*} \alpha_{l} + |u_{l}|^{2} + \frac{1}{2})$$
$$+ p^{2}/2m + V(\mathbf{r}) - \hat{e} \cdot \sum_{l} \nabla V(r) \frac{\hbar}{2MN\omega_{l}}$$
$$\times (\alpha^{\dagger}_{l} + \alpha_{l} - u_{l} - u_{l}^{*}), \quad (26)$$

which will be in diagonal form as far as  $\alpha$  phonons are

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concerned if the coefficient of  $\alpha$  (and  $\alpha_l^{\dagger}$ ) is chosen to vanish. This is the case if

$$u_{l} = \frac{\hat{e} \cdot \nabla V(\mathbf{r})}{(2MNh\omega_{l})^{1/2}}.$$
(27)

 $u_l$  can therefore be interpreted as a mode strain coordinate. Then

$$H = \sum_{l} \hbar \omega_{l} (\alpha_{l} \alpha_{l}^{\dagger} + \frac{1}{2}) + p^{2}/2m + V(\mathbf{r}) - \frac{(\hat{e} \cdot \nabla V(\mathbf{r}))^{2}}{2MN} \sum_{l} \frac{1}{\omega_{l}^{2}}, \quad (28)$$

in which the net effect of the transformation is seen to be an effective single-particle potential deepening inversely proportional to the lattice stiffness. The Hamiltonian is now the sum of the lattice part and a remainder containing the modified anharmonic potential. The ground-state wave function is therefore a product, leading again to a product of f factors.

# **V. HIGH-TEMPERATURE ANHARMONICITY**

In contrast to the deviations from harmonic forces which we have been discussing up to now, the cubic and quartic terms in the expansion of the interatomic potential have their most pronounced effects on observables at high temperatures. In this case, we may use Eq. (5) for f. If the anharmonic corrections V are small in comparison to the harmonic  $H_0$ , then Eq. (5) can be expanded in a power series in V. For a total Hamiltonian

$$H = H_0 + V$$

we obtain, through second order in V, using the notation

$$\langle A \rangle_{0} = \operatorname{Tr}(e^{-\beta H_{0}}A)/\operatorname{Tr}(e^{-\beta H_{0}}), \sqrt{f} = \langle e^{i\mathbf{k}\cdot\mathbf{r}} \rangle_{0} + \langle \beta V \rangle_{0} \langle e^{i\mathbf{k}\cdot\mathbf{r}} \rangle_{0} - \langle \beta V e^{i\mathbf{k}\cdot\mathbf{r}} \rangle_{0} - \langle \beta V \rangle_{0} \langle \beta V e^{i\mathbf{k}\cdot\mathbf{r}} \rangle_{0} + (\langle \beta V \rangle_{0})^{2} \langle e^{i\mathbf{k}\cdot\mathbf{r}} \rangle_{0} - \frac{1}{2} \langle (\beta V)^{2} \rangle_{0} \langle e^{i\mathbf{k}\cdot\mathbf{r}} \rangle_{0} + \frac{1}{2} \langle (\beta V)^{2} e^{i\mathbf{k}\cdot\mathbf{r}} \rangle_{0}.$$

$$(29)$$

Cubic and quartic corrections to the f factor have been calculated by Maradudin and Flinn,<sup>31</sup> and some qualitative features of their results can be understood by inspection of Eq. (29). First, cubic anharmonicity gives no first-order contribution to f. The reason for this is that it is odd in the displacements; thus

$$\langle \beta V \rangle_0 = 0$$
,

and  $\langle \beta V e^{i\mathbf{k}\cdot\mathbf{r}}\rangle_0$  is pure imaginary. The second-order contribution of cubic anharmonicity usually will decrease f, if the second-order terms in Eq. (29) dominate, but might increase it if the imaginary first-order contribution to  $\sqrt{f}$  is large. Quartic anharmonicity, on the other hand, contributes to f in first order, and if it is positive it increases f. Thus, as is often the case, the quartic contribution may overwhelm the cubic. The effects of both cubic and quartic terms are enhanced at elevated temperatures and will disappear at low temperatures unless the zero-point amplitudes are so large that the atoms feel the higher-order terms even at T=0.

#### VI. EXPERIMENTAL SIGNATURES

It is clear that if we know the structure of a crystal and the interatomic forces, then we can in principle calculate the f factor as a function of temperature. It is equally clear that the inverse process is not unique; i.e., many different models will give the same f(T). Nevertheless the approximate separation of f into factors due to the anharmonic and harmonic forces allows one to obtain quantitative gauges of some important parameters, for actual potentials varying within wide limits.

An essential step in the analysis of actual data is the assignment of limits on the temperature dependence of f that are consistent with purely harmonic forces. Housley and Hess<sup>24</sup> have shown that for harmonic forces, the temperature dependence of  $-\ln f$  at high temperatures, which is linear in T, provides a gauge of the force constant of the active atom corresponding to its motion relative to a stationary environment. At lower temperatures, the deviations from the classical dependence will vary according to the harmonic frequency spectrum, but the maximum deviation from classical behavior corresponds to a  $\delta$ -function spectrum, i.e., to the Einstein model. Thus, the temperature variations consistent with a definite slope  $d(-\ln f)/dT$  in the classical region are given by a region lying between the classical and Einstein curves. This is illustrated in Fig. 5.



FIG. 5. Characteristic temperature dependences of the f factor for harmonic, high-temperature anharmonic, and low-temperature anharmonic forces: (a) low-temperature anharmonicity absent; (b) low-temperature anharmonicity present. The shaded regions of each curve correspond to the allowable values of f according to various phonon frequency spectra. In each case, the upper bounds correspond to  $\delta$ -function spectra, while the lower bounds are classical.

If the usual sort of high-temperature anharmonic corrections become important at high T, the deviations from the harmonic curve take the general forms of deviations above or below (usually above) the classical curve of  $-\ln f$  at high temperatures, and such deviations are also illustrated. For the type of low-temperature anharmonicity discussed in this paper, the f factor is reduced below that due to the harmonic forces. The anharmonic term has, for these simple cases, either little or no temperature dependence, particularly in the classical high-temperature region. The harmonic term, however, is subject to the same limits found by Housley and Hess for completely harmonic systems. Therefore, the effect of the low-temperature anharmonicity on  $-\ln f$  is to displace the harmonic curve upward by an amount roughly proportional to the square of the dimension of the flattened central region of the well. The actual behavior of  $-\ln f$  at low temperature will again deviate upward from the classical line, in a manner similar to the curve for a purely harmonic crystal. Such curves have been obtained from detailed studies of FeCl<sub>2</sub>, for example.<sup>28,36</sup> Analysis of the experimental fvalues of FeCl<sub>2</sub>, based upon the present models, yields

<sup>36</sup> D. P. Johnson, thesis, University of Washington, 1967 (unpublished).

estimates of a central flat region that are consistent with an estimate based upon the relative ionic sizes and the known structure.

Thus it has been found that for several models exhibiting low-temperature anharmonicity there is a convenient separation between factors due to anharmonic and harmonic terms. For the high-temperature classical regime, the separation of terms is exact for the rather general types of anharmonic coupling treated here, while at low temperatures complete separation is obtained only for the extremes at which the frequencies of the active atom are much smaller or larger than the frequencies of the dominant normal modes of the crystal. For most physical substances the frequencies are intermediate, and therefore no detailed predictions can be made concerning the low-temperature portions of the curve. Nevertheless, it is likely that the actual low-temperature behavior will have a qualitatively similar shape to the idealized curve shown in Fig. 5, i.e., a deviation tending to exceed the harmonic limit.

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# Erratum

Coupled-Wave Solution of Harmonic Generation in an Optically Active Medium, PAUL P. BEY AND HERBERT RABIN [Phys. Rev. 162, 794 (1967)]. In Eq. (67) the term  $(\omega^2/c)$  should read  $(\omega/c)^2$ .