Localized-Mode Energy Losses in Large Excursions

J. H. WEINER*
Columbia University, New York, New York

(Received 18 March 1966; revised manuscript received 28 September 1966)

During the motion of a defect in a crystal from one equilibrium position to an adjacent one, the associated localized mode (l.m.) undergoes large excursions, and large anharmonic forces are introduced. A new formulation for the resulting mode interaction is presented which appears more appropriate for this process than the usual expansion procedure. It is based on the introduction of curvilinear coordinates in configuration space. One coordinate line, $\mathcal{C}_1$, represents the motion of the system due to the large l.m. excursions, while the effect of the nonlocalized modes (n.l.m.) is to produce small oscillations orthogonal to $\mathcal{C}_1$. Anharmonic effects produce a finite curvature of $\mathcal{C}_1$ and it is shown that the rate of energy transfer from the l.m. to the n.l.m. is proportional to R^{-2}, where R is the radius of curvature of $\mathcal{C}_1$.

1. INTRODUCTION

IF a crystal defect gives rise to a localized mode (l.m.) of vibration, then it is clear that this mode will play an important role in the thermally activated motion of the defect. The localized mode energy is determined by the energy associated with the atoms in the defect vicinity and therefore for the defect to surmount its potential barrier it generally will be necessary that the localized mode have at that time an energy of the order of the barrier energy rather than its equipartition value.

The excited l.m., which gained its excess energy by the anharmonic coupling between modes, will also eventually lose this excess by the same mechanism. The rate at which this loss proceeds has a bearing upon two closely related aspects of defect motion, (1) the heat of transport associated with the motion, and (2) the irreversibility of the process. To fix ideas consider the motion of a vacancy when it interchanges sites with an adjacent atom. As pointed out by Oriani,[1] the vacancy will, in a certain sense, carry the l.m. with it and therefore the energy which this mode retains during the motion will represent an important component of the heat of transport. Secondly, the energy which it retains will determine the probability of the immediate return of the jumping atom to its original site.[2]

For simplicity, we confine attention in this paper to the case in which there is only a single l.m.[3] Then the energy loss of the excited l.m. may be considered to take place in two steps. First there is transfer of energy from the l.m. to the nonlocalized modes (n.l.m.). Initially this rejected energy is contained in a localized wave packet of n.l.m. and is therefore available for return to the l.m. within short times. The energy in this wave packet subsequently spreads out through heat conduction and then may become available for return to the l.m. only after a period of the order of that between jumps. Only the first step in the process is treated here.

The usual method of treating mode interaction is to expand the potential-energy function up to cubic or quartic terms in the normal coordinates and to determine the effect of these anharmonic terms.[4] The large atomic displacements which occur in defect motion may be expected to introduce anharmonic effects which are too severe for such expansion procedures. In this paper, a new formulation is presented which appears more suitable for this process. It corresponds to the use of curvilinear coordinates for configuration space rather than the Cartesian coordinates employed in the expansion procedure. One curvilinear-coordinate line $\mathcal{C}_1$ represents the motion of the system due to the large l.m. excursions, while the effect of the n.l.m. is to produce small oscillations orthogonal to $\mathcal{C}_1$.

In order to motivate the procedure followed, a simple model with two degrees of freedom is described in Sec. 2 which illustrates the physical principles involved. The general curvilinear formulation is developed in Sec. 3. It is employed in Sec. 4, together with some simplifying assumptions, to compute energy transfer from the excited l.m. to the set of n.l.m.

2. MODEL WITH TWO DEGREES OF FREEDOM

We start by consideration of a simple model with two degrees of freedom which illustrates clearly the physical principles involved. It corresponds to a particle of mass m moving in a potential field which, in cylindrical coordinates (r,θ), assumes the form

$$V(r,\theta)=\tfrac{1}{2}\alpha(r-R)^2+\tfrac{1}{2}\beta R^2\theta^2 \quad \text{for} \quad |\theta|\leq\theta_0<\pi, \quad (2.1)$$

where α, β, and R are non-negative constants. Only motions restricted to the stated range of θ are con-

* This work was done while the author was on leave at the Material Mechanics Laboratory, Faculty of Mechanical Engineering, Technion, Haifa, Israel.

[1] R. A. Oriani, in *Thermodynamic and Transport Properties of Gases, Liquids and Solids, ASME* (McGraw-Hill Book Company, Inc., New York, 1963), p. 123; R. A. Oriani, J. Chem. Phys. **34**, 1773 (1961).

[2] S. A. Rice and H. L. Frisch, J. Chem. Phys. **32**, 1026 (1960).

[3] It is possible that in the immediate neighborhood of the stable equilibrium configuration only a single l.m. exists but that others may come into existence during large excursions of the defect. This is the case, for example, in the model employed by J. H. Weiner and W. F. Adler, Phys. Rev. **144**, 511 (1966). This eventuality is not treated in this paper.

[4] See, for example, A. A. Maradudin, Ann. Phys. (N. Y.) **30**, 371 (1964); W. M. Visscher, Phys. Rev. **134**, A965 (1964). These treatments are, however, quantum mechanical, whereas the present one employs only classical mechanics.

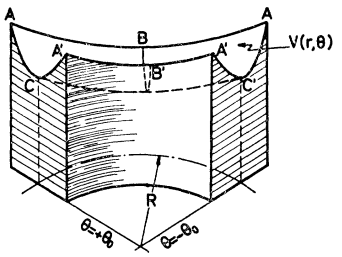

FIG. 1. Potential surface for a model with two degrees of freedom. Potential trough center-line CC' lies in cylindrical surface of radius R. The equation of CC' in cylindrical coordinates is $r=R$, $V=\frac{1}{2}\beta R^2\theta^2$; $|\theta| \leq \theta_0$. The equation of cross sections AA' is $\theta=\pm\theta_0$, $V=\frac{1}{2}\alpha(r-R)^2+\frac{1}{2}\beta R^2\theta_0^2$; the equation of cross section BB' is $\theta=0$, $V=\frac{1}{2}\alpha(r-R)^2$.

sidered, if $\beta\neq 0$. The equations of motion then assume the form

$$\begin{aligned} m\ddot{\theta}+(\beta R^2/r^2)\theta &= (-2m/r)\dot{\theta}\dot{r}\,, \\ m\ddot{r}+\alpha(r-R) &= mr\dot{\theta}^2\,. \end{aligned} \tag{2.2}$$

The model is conveniently visualized as that of a sphere rolling on a curved surface whose height above a plane is given by the function $V(r,\theta)$ of Eq. (2.1), Fig. 1.

If R is infinite there is no coupling between the motions in the r and θ directions. Also for the case, $\beta=0$ and R finite[5] the possibility exists for steady motion in the θ direction with a constant value of $r>R$ so that the potential field force just balances the centrifugal force. However for R finite and $\beta\neq 0$, it is clear that if there is oscillation in the θ direction, motion in the radial direction will be excited. The analogy intended here is between the circumferential mode and a l.m. in a crystal on the one hand and the radial mode and a n.l.m. on the other. Thus, from the present viewpoint, it is the curvature of the potential trough which causes the energy transfer between these modes. This approach may be contrasted with the usual one in which the potential energy function is expanded in a power series in $x=(r-R)\cos\theta$, $y=r\sin\theta$, that is by use of rectangular cartesian coordinates centered at the equilibrium position and directed along the principal axes of the potential energy function there. Then,

$$V(x,y)=\tfrac{1}{2}\alpha x^2+\tfrac{1}{2}\beta y^2+\text{higher order terms}$$

and the coupling between the modes may be ascribed to the cubic and higher order terms. This formulation, however, puts both modes on an equal footing and does not reflect the fact that the anharmonic effects are due primarily to the excursions of the circumferential mode and not to the radial mode.

The analogous situation occurs for a l.m. due to a crystal defect. The anharmonic effects in a crystal increase with the relative atomic displacements from the equilibrium configuration. In a crystal with N atoms, the displacements in the n.l.m. are $O(N^{-1/2})$ while the displacements in a l.m. in the defect vicinity are $O(1)$. Thus with equipartition of energy the contribution of the l.m. to the anharmonic effects is much greater than that of any single n.l.m.[6] This is even more the case during defect motion by thermal activation, when the l.m. has an energy many times its equipartition value.

It therefore appears desirable to develop a formulation for l.m.–n.l.m. interaction by the use of curvilinear coordinates in configuration space analogous to the cylindrical coordinates employed for the model with two degrees of freedom. This is done in the next section.

3. CURVILINEAR COORDINATES FOR CONFIGURATION SPACE

For notational simplicity, we confine our attention here to the case of a linear chain of N identical particles of mass m, although it will be seen that the same type of discussion applies as well to the general, three-dimensional crystal. The equations are first derived in a form valid for arbitrary N. The substantial simplifications possible for N large are introduced subsequently.

Let x_i, $i=1, \cdots, N$ be the displacement of the ith particle from its position in a stable equilibrium configuration and $V(x_1,\cdots,x_N)=V(x)$ the interaction potential energy function. Then, in the absence of external forces, the equations of motion of the system are,

$$m\ddot{x}_i+(\partial V/\partial x_i)=0, \quad i=l, \cdots, N. \tag{3.1}$$

We may regard the configuration space of the system as an N-dimensional Euclidean space with x_i as rectangular cartesian coordinates, that is with metric $ds^2=dx_j dx_j$. Here, and in what follows, unless otherwise indicated the summation convention on repeated indices is employed, with the range of latin indices $1, \cdots, N$. It is convenient to introduce $\mathbf{e}_j$ as a set of N constant unit base vectors for this space directed along the x_j coordinate axes and rewrite Eqs. (3.1) in the form

$$m\ddot{x}_j\mathbf{e}_j+(\partial V/\partial x_j)\mathbf{e}_j=0\,, \tag{3.2a}$$

or

$$m\dot{\mathbf{v}}+\nabla V=0\,, \tag{3.2b}$$

where $\mathbf{x}(t)=x_j(t)\mathbf{e}_j$ is the position vector of the system in configuration space at time t, $\mathbf{v}(t)=\dot{\mathbf{x}}(t)=\dot{x}_j(t)\mathbf{e}_j$ is its velocity and $\nabla=(\partial/\partial x_j)\mathbf{e}_j$ is the gradient operator.

Let $V_{ij}(x)=(\partial^2 V(x)/\partial x_i\partial x_j)$ be the matrix of second partials of the potential energy function with orthonormal eigenvectors $\mathbf{a}_i(x)$. We are concerned here with the case in which the chain contains an imperfection (e.g., a vacancy or dislocation) which gives rise to a single localized eigenvector $\mathbf{a}_1(x)$, i.e., one whose components are small except for atoms in the neighborhood of

[5] This then becomes the model introduced by D. Bohm and G. Carmi, Phys. Rev. **133**, A319 (1964).

[6] On the other hand, the number of n.l.m. is $O(N)$ and, as shown by H. B. Rosenstock and C. C. Klick, Phys. Rev. **119**, 1198 (1960), their collective effect on the relative atomic displacements in the defect vicinity is of the same order of magnitude as that of the single l.m.

the defect. Furthermore, we assume that at some reference time $t=0$, when the system is passing through the stable equilibrium position, this mode is highly excited. It may be expected that the system subsequently will undergo large excursions along the path $\mathcal{C}_1$, where $\mathcal{C}_1$ is the curve[7] passing through $\mathbf{x}=0$ and tangent to $\mathbf{a}_1(x)$, with the motion of the n.l.m. producing small vibrations orthogonal to this path. It is therefore desirable to introduce a curvilinear coordinate system for the region in configuration space in the neighborhood of $\mathcal{C}_1$, which has $\mathcal{C}_1$ as one of the coordinate lines, with rectangular cartesian coordinates directed along $\mathbf{a}_\alpha(x)$, $\alpha=2, \cdots, N$ in the hyperplane perpendicular to $\mathcal{C}_1$ at $\mathbf{x}$. In what follows the summation convention is employed as well with respect to Greek indices which consistently have the range 2, $\cdots$, N. Repeated indices in parentheses, however, do not participate in the summation convention.

Let s_1 denote distance measured along $\mathcal{C}_1$ from the stable equilibrium configuration. Then the parametric equations $\mathbf{x}(s_1)$ for $\mathcal{C}_1$ are the solutions to the system of ordinary differential equations

$$d\mathbf{x}/ds_1=\mathbf{a}_1(x); \quad \mathbf{x}(0)=\mathbf{0}. \tag{3.3}$$

Since the $\mathbf{a}_i(x)$ are unit vectors it follows that we may write

$$d\mathbf{a}_1/ds_1=\mathbf{n}/R, \tag{3.4}$$

where $\mathbf{n}(s_1)$ is a unit vector orthogonal to $\mathcal{C}_1$ and, in analogy to the 3-dimensional case $R(s_1)$ may be referred to as the radius of curvature of $\mathcal{C}_1$ at s_1. Explicitly,

$$R^{-2}(s_1)=\frac{d^2\mathbf{x}(s_1)}{ds_1^2}\cdot\frac{d^2\mathbf{x}(s_1)}{ds_1^2}=\frac{d^2x_i(s_1)}{ds_1^2}\frac{d^2x_i(s_1)}{ds_1^2}. \tag{3.5}$$

It is now possible to introduce the coordinate θ as the solution to the differential equation

$$d\theta/ds_1=1/R(s_1), \tag{3.6}$$

where θ plays the role of the angular coordinate and is taken as constant on any hyperplane $\mathcal{P}$ perpendicular to $\mathcal{C}_1$. We now denote the eigenvectors of $V_{ij}(x)$ for a point on $\mathcal{C}_1$ corresponding to θ by $\mathbf{a}_i(\theta)$ and take the set $\mathbf{a}_\alpha(\theta)$ as the constant base vectors for a rectangular cartesian coordinate system for $\mathcal{P}$. This system is denoted by s_α, with $s_\alpha=0$ corresponding to $\mathcal{C}_1$, and the full curvilinear coordinate system for the portion of configuration space of interest is then given by the variables $(\theta,s_2,\cdots,s_N)$, denoted in brief by (θ,s).

Let $\boldsymbol{\xi}(\theta)$ be the vector from an arbitrary reference point $\mathbf{0}$ to the point A on $\mathcal{C}_1$ corresponding to θ. Let $\mathcal{P}$ be the hyperplane through A, and $\mathbf{s}$ the vector from A to an arbitrary point B in $\mathcal{P}$. Then the vector $\boldsymbol{\varrho}$ from $\mathbf{0}$ to B is

$$\boldsymbol{\varrho}=\boldsymbol{\xi}(\theta)+\mathbf{s}=\boldsymbol{\xi}(\theta)+s_\alpha\mathbf{a}_\alpha(\theta). \tag{3.7}$$

If the motion of a system is given by the functions $\theta(t)$, $s_\alpha(t)$, its velocity is

$$\begin{aligned}\mathbf{v}=\dot{\boldsymbol{\varrho}}&=\partial\boldsymbol{\xi}/\partial t+\dot{s}_\alpha\mathbf{a}_\alpha+s_\alpha\dot{\mathbf{a}}_\alpha\\&=\left(\frac{d\boldsymbol{\xi}}{d\theta}+s_\alpha\frac{d\mathbf{a}_\alpha}{d\theta}\right)\dot{\theta}+\dot{s}_\alpha\mathbf{a}_\alpha.\end{aligned} \tag{3.8}$$

From Eqs. (3.3) and (3.6) it is seen that

$$d\boldsymbol{\xi}/d\theta=R\mathbf{a}_1.$$

We may express $d\mathbf{a}_i/d\theta$ in terms of $\mathbf{a}_j(\theta)$ as

$$\frac{d\mathbf{a}_i}{d\theta}=\omega_{ij}\mathbf{a}_j; \quad \omega_{ij}=\frac{d\mathbf{a}_i}{d\theta}\cdot a_j=\frac{-d\mathbf{a}_j}{d\theta}\cdot\mathbf{a}_i=-\omega_{ji}, \tag{3.9}$$

where the antisymmetry of the matrix ω_{ij} follows from the orthonormality of the vectors $\mathbf{a}_i$. In particular, by use of Eqs. (3.4) and (3.6),

$$\omega_{1\alpha}=(d\mathbf{a}_1/d\theta)\cdot\mathbf{a}_\alpha=\mathbf{n}\cdot\mathbf{a}_\alpha=n_\alpha. \tag{3.10}$$

We may now write the system velocity as

$$\begin{aligned}\mathbf{v}&=(R+s_\alpha\omega_{\alpha1})\dot{\theta}\mathbf{a}_1+(\dot{s}_\alpha+s_\beta\omega_{\beta\alpha}\dot{\theta})\mathbf{a}_\alpha\\&=r\dot{\theta}\mathbf{a}_1+(\dot{s}_\alpha+s_\beta\omega_{\beta\alpha}\dot{\theta})\mathbf{a}_\alpha=v_i\mathbf{a}_i,\end{aligned} \tag{3.11}$$

where

$$r(\theta,s)=R-s_\alpha\omega_{1\alpha}=R-\mathbf{s}\cdot\mathbf{n}, \tag{3.12}$$

and is thus the distance of the point D, the projection of B on $\mathbf{n}$, from the local center of curvature C of $\mathcal{C}_1$ (Fig. 2).

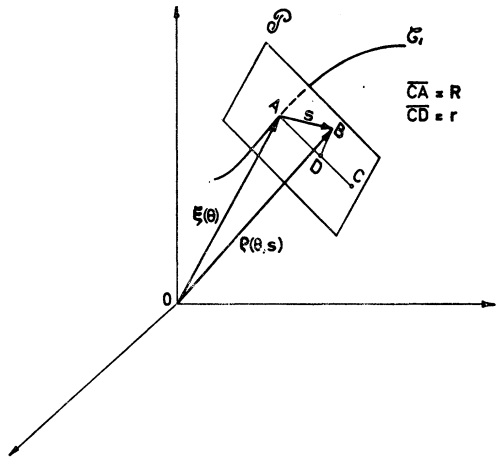

FIG. 2. Curvilinear coordinate system in N-dimensional configuration space. $\mathcal{C}_1$ is the curve which passes through the stable equilibrium configuration and is everywhere tangent to the eigenvector $\mathbf{a}_1(x)$. The hyperplane $\mathcal{P}$ is spanned by the remaining eigenvectors, $\mathbf{a}_\alpha(x)$, and is thus orthogonal to $\mathcal{C}_1$. Remaining quantities are defined in text, from Eq. (3.4) to Eq. (3.12).

[7] That is, the vector field $\mathbf{a}_1(x)$ gives rise to a congruence of curves in configuration space such that the curve of the congruence passing through the point $\mathbf{x}$ is there tangent to the vector $\mathbf{a}_1(x)$. The curve $\mathcal{C}_1$ is then the particular curve of the congruence which passes through $\mathbf{x}=0$. Note that from the present viewpoint anharmonic effects exhibit themselves through the variation of the eigenvectors $\mathbf{a}_i(x)$ with position and in their absence $\mathcal{C}_1$ is a straight line.

Thus far all quantities have been referred to the local orthonormal frame $\mathbf{a}_i(\theta)$ and accordingly all indices have been written as covariant indices. In order to express the gradient operator in the (θ,s) system, it will be convenient to consider here the covariant and contravariant base vectors $\mathbf{g}_i$ and $\mathbf{g}^i$, respectively. From Eqs. (3.7), (3.9), and (3.12),

$$\mathbf{g}_1=\partial\varrho/\partial\theta=R\mathbf{a}_1+s_\alpha d\mathbf{a}_\alpha/d\theta=R\mathbf{a}_1+s_\alpha\omega_{\alpha i}\mathbf{a}_i$$
$$=r\mathbf{a}_1+s_\alpha\omega_{\alpha\beta}\mathbf{a}_\beta, \quad (3.13)$$
$$\mathbf{g}_\alpha=\partial\varrho/\partial s_\alpha=\mathbf{a}_\alpha.$$

The contravariant base vectors $\mathbf{g}^i$ may be found most readily by use of the relations

$$\mathbf{g}^i\cdot\mathbf{g}_j=\delta_j{}^i,$$

where $\delta_j{}^i$ is the Kronecker delta. The results are

$$\mathbf{g}^1=\mathbf{a}_1/r;\ \mathbf{g}^\alpha=\mathbf{a}_\alpha-(s_\beta\omega_{\beta\alpha}\mathbf{a}_1/r). \quad (3.14)$$

The gradient operator ∇ is then

$$\frac{\partial}{\partial\theta}\mathbf{g}^1+\frac{\partial}{\partial s_\alpha}\mathbf{g}^\alpha=\frac{1}{r}\left(\frac{\partial}{\partial\theta}-s_\beta\omega_{\beta\alpha}\frac{\partial}{\partial s_\alpha}\right)\mathbf{a}_1+\frac{\partial}{\partial s_\alpha}\mathbf{a}_\alpha. \quad (3.15)$$

By use of Eqs. (3.11) and (3.15) the equations of motion, Eq. (3.2), may now be rewritten as

$$m\dot v_1+\frac{1}{r}\frac{\partial V}{\partial\theta}-\frac{s_\beta\omega_{\beta\alpha}}{r}\frac{\partial V}{\partial s_\alpha}=-mv_\alpha\omega_{\alpha1}\dot\theta=mv_\alpha n_\alpha\dot\theta, \quad (3.16a)$$

$$m\dot v_\alpha+\frac{\partial V}{\partial s_\alpha}=-mv_i\omega_{i\alpha}\dot\theta=-mr(\dot\theta)^2n_\alpha-mv_\beta\omega_{\beta\alpha}\dot\theta. \quad (3.16b)$$

The curvilinear-coordinate formulation of Eqs. (3.16) may be contrasted with the expansion formulation obtained by expanding the potential energy function to cubic terms. The latter leads to a Hamiltonian of the form

$$H=H_0+H_C,$$

where

$$H_0=\tfrac{1}{2}\textstyle\sum_k(P_k{}^2/m+\lambda_{(k)}Q_{(k)}{}^2),$$
$$V_C=\tfrac{1}{3}\textstyle\sum_{ijk}A_{ijk}Q_iQ_jQ_k, \quad (3.17)$$

where the coefficients A_{ijk} may be taken as completely symmetric. This leads to the system of equations of motion

$$m\ddot Q_i+\lambda_{(i)}Q_{(i)}=\textstyle\sum_{jk}A_{ijk}Q_jQ_k. \quad (3.18)$$

In the curvilinear-coordinate formulation the right-hand forcing terms depend primarily upon velocities whereas in the expansion procedure they depend only upon the coordinates. Also, and what is more significant, in the expansion formulation the total energy to be ascribed to the modes, H_0, does not remain strictly constant during the motion; this is only the case for the total energy H. This makes it possible, in the expansion procedure, to speak of energy transfer between modes only for the case in which the coupling energy V_C is very small compared to the mode energy H_0.

On the other hand for the region surrounding $\mathcal{C}_1$ for which the (θ,s) coordinate system is allowable, the curvilinear coordinate formulation is fully equivalent to the original equations of motion, Eq. (3.1), no other assumptions having been made. In particular, the conservation of energy of the system may be derived from it by multiplication of Eq. (3.16a) by v_1 and Eq. (3.16b) by v_α and summing. If use is made of the expressions for v_i, Eq. (3.11), and of the antisymmetry of ω_{ij}, the expected result

$$\frac{d}{dt}\left(\frac{m}{2}\dot v_i\dot v_i+V\right)=-mv_iv_j\omega_{ij}\dot\theta=0 \quad (3.19)$$

is obtained. If, therefore, the potential-energy function takes the form

$$V(\theta,s)=V_1(\theta)+\textstyle\sum_\alpha V_\alpha(s_\alpha), \quad (3.20)$$

then Eq. (3.19) may be interpreted as expressing the conservation of the sum of the energies to be ascribed to the individual modes. The terms on the right-hand side of Eqs. (3.16) then represent the interaction terms which produce energy transfer between these modes. In particular, the role of the "centrifugal force," $-mr(\dot\theta)^2$, in transferring energy into the n.l.m. is completely analogous to that in the two-dimensional model of Sec. 2.

We consider next the simplifications permissible for large N and show first that for this case and small n.l.m. excursions, the potential-energy function $V(\theta,s)$ can be put in the separated form of Eq. (3.20). For a point on $\mathcal{C}_1$ at distance s_1, the value of $(\partial V/\partial x_i)(s_1)$ may be determined by integration along $\mathcal{C}_1$ from the stable equilibrium configuration at the origin. If use is made of the fact that $\mathcal{C}_1$ has as unit tangent vector the eigenvector $\mathbf{a}_1=a_{1i}\mathbf{e}_i$ of the matrix V_{ij}, it follows that

$$\frac{\partial V}{\partial x_i}(s_1)=\int_0^{s_1}\frac{d}{d\sigma_1}\frac{\partial V}{\partial x_i}(\sigma_1)d\sigma_1=\int_0^{s_1}\frac{\partial^2V}{\partial x_i\partial x_j}\frac{\partial x_j}{\partial\sigma_1}d\sigma_1$$
$$=\int_0^{s_1}V_{ij}a_{1j}d\sigma_1=\int_0^{s_1}\lambda_1(\sigma_1)a_{1i}(\sigma_1)d\sigma_1, \quad (3.21)$$

where $\lambda_1(\sigma_1)$ is the eigenvalue of $V_{ij}(\sigma_1)$ corresponding to $\mathbf{a}_1(\sigma_1)$. Also, at any point on $\mathcal{C}_1$ the unit vector tangent to the s_α coordinate line is $\mathbf{a}_\alpha=a_{\alpha j}\mathbf{e}_j$. Therefore,

$$\frac{\partial V}{\partial s_\alpha}(s_1)=\frac{\partial V}{\partial x_i}(s_1)a_{\alpha i}(s_1)=\int_0^{s_1}\lambda_1(\sigma_1)a_{\alpha i}(s_1)a_{1i}(\sigma_1)d\sigma_1, \quad (3.22)$$

and

$$\left|\frac{\partial V}{\partial s_\alpha}(s_1)\right|\le\lambda_{1,\max}s_1M, \quad (3.23)$$

where $\lambda_{1,\max}$ is an upper bound for $\lambda_1(\sigma_1)$ and M is

chosen so that

$$|a_{\alpha i}(s_1)a_{1i}(\sigma_1)| \leq |a_{\alpha i}(s_1)|_{\max} \sum_i |a_{1i}(\sigma_1)| \leq M$$

for

$$0 \leq \sigma_1 \leq s_1.$$

However, since $\mathbf{a}_\alpha$ is a n.l.m. and $\mathbf{a}_1$ is a l.m., we may expect that as $N \to \infty$

$$|a_{\alpha i}| = 0(N^{-1/2}); \quad \sum_i |a_{1i}| = 0(1),$$

i.e., that the l.m. is sufficiently localized so that the infinite series converges. It follows that M and therefore $|(\partial V/\partial s_\alpha)(s_1)|$ can be made arbitrarily small by taking N sufficiently large and, in what follows, it will be taken as zero. Physically, the calculation reflects the fact that the additional perturbation of the lattice due to the l.m. excursion has little effect on most of the lattice and therefore little effect upon characteristics of the n.l.m. For this reason, it is also to be expected that $\lambda_\alpha(s_1)$, the eigenvalues of $V_{ij}(s_1)$ corresponding to the n.l.m., will have negligible dependence upon s_1 and, in what follows, will be taken as constants. Finally, since x_i is linear in the coordinates s_α, and the latter are chosen in characteristic directions of the matrix $V_{ij} = \partial^2 V/\partial x_i \partial x_j$, it follows that

$$\partial^2 V/\partial s_\alpha \partial s_\beta = V_{ij} a_{\alpha i} a_{\beta j} = \lambda_{(\alpha)} \delta_{(\alpha)\beta}. \tag{3.24}$$

If attention is therefore restricted to sufficiently small n.l.m. excursions, so that cubic terms and higher in s_α may be neglected, the expansion of $V(\theta,s)$ takes the separated form

$$V(\theta,s) = F(\theta) + \tfrac{1}{2} \sum_\alpha \lambda_\alpha s_\alpha^2. \tag{3.25}$$

As a further simplification for large N we note that we may expect that the derivatives $da_{\alpha i}/d\theta$ will be negligible except for a limited number of values of i corresponding to atoms in the vicinity of the defect. Since $|a_{\beta i}| = 0(N^{-1/2})$, it follows from the definition of $\omega_{\alpha\beta}$ [Eq. (3.9)] that the quantities $\omega_{\alpha\beta}$ will be small for large N and may be taken as zero[8] for that case. The equations (3.16) then take the form

$$m\dot{v}_1 + (1/r)\partial F/\partial\theta = m\dot{s}_\alpha n_\alpha \dot{\theta}, \tag{3.26a}$$

$$m\ddot{s}_\alpha + \lambda_{(\alpha)} s_{(\alpha)} = -mr\dot{\theta}^2 n_\alpha. \tag{3.26b}$$

These equations are also seen to imply the conservation of the sum of the energies assigned to the individual modes, that is,

$$\frac{d}{dt}[\tfrac{1}{2}(mv_1^2 + F(\theta)) + \tfrac{1}{2}\textstyle\sum_\alpha (m\dot{s}_\alpha^2 + \lambda_{(\alpha)} s_{(\alpha)}^2)] = 0. \tag{3.27}$$

[8] This means that there is no twist of the frame $\mathbf{a}_\alpha(\theta)$ along $\mathcal{C}_1$. The (θ,s) coordinate system then becomes orthogonal curvilinear.

4. ENERGY TRANSFER

With some additional simplifications, we may use Eq. (3.26) to estimate the amount of energy transferred from the l.m. to each of the n.l.m. First of all we restrict attention to the case in which the amplitudes of motion of the n.l.m. are small compared to the radius of curvature of $\mathcal{C}_1$, i.e., $|s_\alpha(t)| \ll R$. Then, as a first approximation, we replace r by R in Eq. (3.26b) so that its r.h.s. is now a function of θ only. We further restrict attention to such time intervals and strengths of interaction that the perturbation in $\theta(t)$ due to the energy loss to the n.l.m. may be neglected in the r.h.s. of Eq. (3.26b). Then these equations take the form

$$\ddot{s}_\alpha + \omega_{(\alpha)}^2 s_{(\alpha)} = h_\alpha(t), \quad \omega_\alpha^2 = \lambda_\alpha/m, \tag{4.1}$$

where

$$h_\alpha(t) = -n_\alpha R\dot{\theta}^2 \tag{4.2}$$

may be regarded as a prescribed function of time. Denote by $t=0$ the time at which we begin to examine the interaction of the l.m. with all the n.l.m. At this time we assume that the l.m. has an energy E_1, greatly in excess of the equipartition value and we examine its interaction with an ensemble of n.l.m., where the distribution of this ensemble corresponds at $t=0$ to thermal equilibrium. As the coordinates for the phase space of the α mode we use its energy E_α and phase φ_α. Then for thermal equilibrium its distribution function $\rho_\alpha(E_\alpha,\varphi_\alpha)$ in this phase space corresponds to a random-phase distribution, that is,

$$\rho_\alpha(E_\alpha,\varphi_\alpha) = \rho_\alpha(E_\alpha), \tag{4.3}$$

and

$$\langle E_\alpha \rangle_{t=0} = \int_0^\infty E_\alpha \rho_\alpha(E_\alpha) dE_\alpha = kT. \tag{4.4}$$

A typical member of the ensemble, with energy E_α and phase φ_α at $t=0$ therefore has initial conditions

$$\begin{aligned} s_\alpha(0) &= (2E_\alpha/\lambda_\alpha)^{1/2} \sin\varphi_\alpha, \\ \dot{s}_\alpha(0) &= (2E_\alpha/m)^{1/2} \cos\varphi_\alpha, \end{aligned} \tag{4.5}$$

and has its subsequent motion controlled by Eq. (4.1). Therefore,

$$s_\alpha(t) = (2E_\alpha/\lambda_\alpha)^{1/2} \sin(\omega_\alpha t + \varphi_\alpha) + H_\alpha(t), \tag{4.6}$$

where

$$H_\alpha(t) = \frac{1}{\omega_\alpha} \int_0^t h_\alpha(\tau) \sin\omega_\alpha(t-\tau) d\tau. \tag{4.7}$$

It then follows, because of the initial random distribution in phase, that

$$\langle E_\alpha \rangle_{t=t} = kT + E_\alpha'(t), \tag{4.8}$$

where E_α', the energy transferred to the α mode, is

$$2E_\alpha'/m=\dot{H}_\alpha^2+\omega_\alpha^2 H_\alpha^2$$
$$=\left(\int_0^t h_{(\alpha)}(\tau)\,\sin\omega_{(\alpha)}(t-\tau)d\tau\right)^2+\left(\int_0^t h_{(\alpha)}(\tau)\,\cos\omega_{(\alpha)}(t-\tau)d\tau\right)^2$$
$$=\left(\int_0^t h_{(\alpha)}(\tau)\,\sin\omega_{(\alpha)}\tau d\tau\right)^2+\left(\int_0^t h_{(\alpha)}(\tau)\,\cos\omega_{(\alpha)}\tau d\tau\right)^2, \quad (4.9)$$

and where the change in argument of the trigonometric functions may be seen by first rewriting the squares of the integrals as iterated integrals and then applying trigonometric identities. It is seen that to the present degree of approximation, the energy transferred from the l.m. to the n.l.m. is independent of the temperature of the latter. In order to make the calculation of E_α' more explicit, we introduce the additional simplifying assumptions that n_α and R are constant and that

$$F(\theta)=\tfrac{1}{2}\lambda_1 R^2\theta^2. \quad (4.10)$$

Then, with the approximations that $r\sim R$ and that the effects of the interactions on $\theta(t)$ are neglected,

$$\theta(t)=R^{-1}(2E_1/\lambda_1)^{1/2}\sin\omega_1 t, \quad (4.11)$$

$$h_\alpha(t)=(-2n_\alpha E_1/mR)\,\cos^2\omega_1 t. \quad (4.12)$$

Let

$$\bar{t}=\omega_1 t;\quad \bar{\omega}_\alpha=\omega_\alpha/\omega_1. \quad (4.13)$$

Then substitution of Eqs. (4.12) and (4.13) into Eq. (4.9) leads to the result

$$E_\alpha'/E_1=(2n_\alpha^2 E_1/mR^2\omega_1^2)g_\alpha(\bar{t}), \quad (4.14)$$

where

$$g_\alpha(\bar{t})=\left(\int_0^{\bar{t}}\cos^2\tau\,\sin\bar{\omega}_\alpha\tau d\tau\right)^2+\left(\int_0^{\bar{t}}\cos^2\tau\,\cos\bar{\omega}_\alpha\tau d\tau\right)^2$$
$$=\frac{7\bar{\omega}_\alpha^2-12}{8(\bar{\omega}_\alpha^2-4)^2}+\frac{1}{2\bar{\omega}_\alpha^2}-\frac{(\bar{\omega}_\alpha^2-2)}{2\bar{\omega}_\alpha(\bar{\omega}_\alpha^2-4)(\bar{\omega}_\alpha-2)}$$
$$\times\cos(\bar{\omega}_\alpha-2)t-\frac{(\bar{\omega}_\alpha^2-2)}{2\bar{\omega}_\alpha(\bar{\omega}_\alpha^2-4)(\bar{\omega}_\alpha+2)}\cos(\bar{\omega}_\alpha+2)t$$
$$-\frac{(\bar{\omega}_\alpha^2-2)}{\bar{\omega}_\alpha^2(\bar{\omega}_\alpha^2-4)}\cos\bar{\omega}_\alpha t+\frac{1}{8(\bar{\omega}_\alpha^2-4)}\cos 4t$$
$$+\frac{1}{2(\bar{\omega}_\alpha^2-4)}\cos 2t. \quad (4.15)$$

As an approximation for the case in which the l.m. frequency is very high compared to the n.l.m. frequencies, i.e. $\bar{\omega}_\alpha\ll 1$, it is found that

$$\lim_{\bar{\omega}_\alpha\to 0} g_\alpha(\bar{t})=\tfrac{1}{4}[\bar{t}^2+\bar{t}\sin 2\bar{t}+\tfrac{1}{4}\sin^2 2\bar{t}]. \quad (4.16)$$

The energy transfer $\Delta E_\alpha'$ per half-period of the l.m. is then given by

$$\Delta E_\alpha'/E_1=n_\alpha^2 E_1\pi^2/2mR^2\omega_1^2 \quad (4.17)$$

and the total energy transferred by the l.m. per half-period, $\Delta E'=\sum_\alpha \Delta E_\alpha'$ is

$$\Delta E'/E_1=E_1\pi^2/2mR^2\omega_1^2. \quad (4.18)$$

It is also seen from Eq. (4.15) that a resonance occurs if there exists a n.l.m. with $\bar{\omega}_\alpha=2$, that is with a frequency twice that of the l.m. In this case this particular $g_\alpha(\bar{t})$ takes the form

$$g_\alpha(\bar{t})=\tfrac{1}{16}[\bar{t}^2+\tfrac{1}{2}\bar{t}\sin 4\bar{t}+2\bar{t}\sin 2\bar{t}$$
$$-5/4\sin^2 2\bar{t}-\sin^2\bar{t}]. \quad (4.19)$$

5. CONCLUSIONS

The new curvilinear-coordinate formulation presented for energy transfer between a localized mode and the set of nonlocalized modes appears more suitable for the study of strong anharmonic forces, when the latter are due to large excursions of the localized mode, than the usual expansion procedure. With additional simplifying assumptions, this formulation has been employed to compute expressions for this energy transfer. The emphasis of the paper has been on the process of defect motion, but the formulation may also be of use for other problems of mode interaction. The present treatment however, is completely classical and therefore is only valid at temperature levels sufficiently high so that quantum effects are unimportant.

ACKNOWLEDGMENTS

This work was done while the author was on leave as Guggenheim Fellow and Fulbright Research Scholar at the Material Mechanics Laboratory, Faculty of Mechanical Engineering, of the Technion in Israel. He finds it a pleasure to thank its director, Professor Sol R. Bodner for his unstinted hospitality and for helpful discussions. The efficient assistance of its secretary, Mrs. Reuben Hammer is also gratefully acknowledged.