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Phonon Spectral Functions and Ground-State Energy of Quantum Crystals in Perturbation Theory with a Variationally Optimum Correlated Basis Set

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A theory is presented of the damping and frequency shift of phonons and of the ground-state energy corrections due to interactions between phonons in quantum crystals with singular forces. The technique begins with the adoption of a trial ground-state wave function of the Jastrow form, together with trial excited-state wave functions constructed to represent one-, two-, and three-phonon excitations. The Hamiltonian matrix in this restricted basis is diagonalized, and the basis is optimized by minimizing the lowest eigenvalue with respect to variational phonon parameters. Using a lowest-order cluster expansion, the unambiguous prescription is obtained that a specific effective potential, softened by the Jastrow correlation function, replaces everywhere the true potential in the existing self-consistent theory of phonon damping applicable to nonsingular forces. Close analogies are drawn with the correlated basis function treatment of superfluid liquid helium.

I. INTRODUCTION

One of the leading unresolved questions in the area of the lattice dynamics of quantum crystals which is presently receiving considerable research attention[1–4] is that of the role played by short-range correlations in the interactions between phonons. In a crystal where the forces between atoms are weak and completely regular everywhere, the description of the scattering of phonons from each other due to the residual anharmonicity, and of the resulting decay rates and frequency shifts of the vibrational modes, has already been well established.[5–10] A variety of alternative mathemathical techniques has been developed for arriving at this description. In a quantum crystal such as helium, however, not only are the forces very strongly repulsive at small interatomic separations, but more importantly, separations of such small size would be physically realized with substantial probability if the forces were not strong, because of the exceptionally large vibrational zero-point motion. Thus, it is vital in treating a material such as solid helium to take explicit account of the short-range correlations by which dynamical configurations of high potential energy are avoided, configurations which would otherwise be favored from zero-point kinetic energy considerations alone.

The effect of correlations due to short-range repulsion on the frequencies of phonons, considered approximately as free noninteracting modes, has already been the subject of considerable investigation.[11-15] While this question is by no means completely settled, it is probably fair to say that consistent results are being converged upon from differing viewpoints which are qualitatively reasonable and semiquantitatively satisfactory. However, it is generally conceded that corrections to these descriptions arising from interactions between phonons could well be sizable, and that estimates of these corrections based on simple physical reasoning and educated intuition are not entirely reliable. It has thus become of critical importance to develop a careful and systematic treatment of phonon interactions including the effects of short-range correlations, so that present theoretical approximations starting from noninteracting phonons can achieve an additional measure of credibility and so that comparison with experimental data[16,17] can be used as a fully meaningful test of computations.

In surveying the techniques which have been used previously to treat the lowest-order noninteracting phonon approximation, we find that the scheme of Koehler[13,18] is the one which is most readily extendible to include phonon interactions. The Koehler scheme to lowest order can be viewed strictly as a variational one in which a trial ground-state wave function for the crystal is exhibited explicitly, and the expectation value of the Hamiltonian in the trial state is minimized with respect to a set of variational parameters. The trial wave function is chosen to be in the form of a product of pair functions:

$$\Psi_0(\vec{r}_1,\ldots,\vec{r}_N)=\tilde{\Psi}(\vec{r}_1,\ldots,\vec{r}_N)\exp\left(-\sum_{i<j}\frac{1}{4}\,\vec{u}_{ij}\cdot\overleftrightarrow{\Gamma}_{ij}\cdot\vec{u}_{ij}\right)\Big/$$

$$\left[\int d^{3N}r\,|\tilde{\Psi}(\vec{r}_1,\ldots,\vec{r}_N)|^2 \exp\left(-\sum_{i<j}\frac{1}{2}\,\vec{u}_{ij}\cdot\overleftrightarrow{\Gamma}_{ij}\cdot\vec{u}_{ij}\right)\right]^{1/2} , \tag{1.1}$$

$$\tilde{\Psi}(\vec{r}_1,\ldots,\vec{r}_N)\equiv\prod_{i<j} f_{ij}(\vec{r}_{ij}) , \tag{1.2}$$

where the $\vec{r}_{ij}$ are coordinate differences,

$$\vec{r}_{ij}\equiv\vec{r}_i-\vec{r}_j , \tag{1.3}$$

$$\vec{u}_{ij}\equiv\vec{r}_{ij}-\vec{R}_{ij} , \tag{1.4}$$

are displacement differences from mean lattice sites $\vec{R}_i$ which form a regular crystalline array. The Gaussian factor in Ψ_0 is just the ground-state wave function which would obtain for some quasiharmonic crystal whose force constants (or oscillator frequencies) are dependent on the particular choice of coefficients $\overleftrightarrow{\Gamma}_{ij}$. The factor $\tilde{\Psi}$ is of the so-called Jastrow type, containing pair functions $f(\vec{r})$ chosen[19] to take account of the strong short-range repulsion between atoms. These Jastrow functions are required to tend rapidly to 0 for small interparticle separations and to unity for large separations:

$$\begin{aligned} f_{ij}(\vec{r}) &\to 0, \quad \vec{r}\to 0 \\ &\to 1, \quad \vec{r}\to\infty . \end{aligned} \tag{1.5}$$

It is then possible to evaluate the trial ground-state energy,

$$E_0\equiv(\Psi_0,\mathcal{H}\Psi_0) , \tag{1.6}$$

for a Hamiltonian

$$\mathcal{H}=\sum_i \frac{p_i^2}{2M_i}+\frac{1}{2}\sum_{i,j} v_{ij}(\vec{r}_{ij}) \tag{1.7}$$

of particles interacting by pair potentials $V_{ij}(\vec{r}_{ij})$. The coefficients $\overleftrightarrow{\Gamma}_{ij}$ are to be determined by requiring that E_0 be stationary with respect to variations of the $\overleftrightarrow{\Gamma}_{ij}$.

Since the Gaussian function

$$\exp\left(-\sum_{i<j}\frac{1}{2}\,\vec{u}_{ij}\cdot\overleftrightarrow{\Gamma}_{ij}\cdot\vec{u}_{ij}\right)$$

is the exact ground-state wave function for some quasiharmonic crystal, the phonon frequencies and polarization vectors of that crystal can be expressed in terms of the matrices $\overleftrightarrow{\Gamma}_{ij}$. In the absence of strong short-range repulsion, with v everywhere weak and $f\to 1$, these frequencies are also given by the inverse eigenvalues of the displacement correlation function,

$$\overleftrightarrow{D}_{ij}\equiv(\Psi_0,\vec{u}_i\vec{u}_j\,\Psi_0) . \tag{1.8}$$

However, when short-range correlations are present the equivalence of these two definitions of the phonon frequencies no longer holds; it is preferable to continue the interpretation of the phonon frequencies as taken from the displacement correlation. Again in the absence of short-range correlations, the phonon frequencies and polarization vectors determined in this way are identical to those of the first-order self-consistent phonon approximation[20] derived by a variety of other mathematical techniques.

Although the variational approach is the neatest and most compact way to obtain the self-consistent phonon results summarized above, the development originally proposed[18] by Koehler is the more useful when investigating generalizations. Koehler suggested the display of not just a ground-state wave function, but in addition a set of low-lying excited states as well. These excited states are interpreted as differing from the ground state by the excitation of one or more phonons. Since it is argued that the lowest-lying excitations should not interfere with the short-range repulsive correlations, which involve dynamics of much higher excitation energy, the excited states are exhibited in the form of low-order polynomials in the displacement variables multiplied into the ground-state wave function. The Jastrow product is thus assumed to remain unchanged from ground state to low excited states. The coefficients in the polynomials are chosen to make the states orthonormal. Matrix elements of the Hamiltonian in the phonon basis states can readily be evaluated and a full Hamiltonian matrix exhibited rather than just the ground-state expectation value. The remarkable feature of this matrix, pointed out by Koehler, is that the stationary variation condition on E_0 is identical to the condition of the vanishing of those matrix elements of $\mathcal{H}$ between the ground state and all two-phonon excited states. A further result is that when this condition is satisfied the excitation frequency of the one-phonon state is precisely the same as the inverse eigenfrequency of the displacement correlation function. This important equivalence gives added support to the interpretation of the constructed basis set as representing phonon excitations and also of the ground-state displacement correlation as the proper source for phonon eigenfrequencies.

The original Koehler viewpoint, that of the evaluation of a Hamiltonian matrix with respect to an explicitly constructed basis set representing ground-state and low-lying excitations, is one which lends itself naturally to a sequence of generalizations. If the lowest-order self-consistent phonon approximation is equivalent to the diagonalization of $\mathcal{H}$ in the zero- and one-phonon subset, with subsidiary condition of vanishing matrix elements between zero- and two-phonon states, then in the next order of approximation $\mathcal{H}$ can be diagonalized in the larger subset of zero-, one-, and two-phonon states. Successively higher approximations can be generated by enlarging the subspace in which $\mathcal{H}$ is diagonalized to include states with successively larger numbers of phonons. It is just this generalized approach which we propose to develop in more detail in the present paper and which we will show leads to systematic, unambiguous, and easily computable formulas for phonon spectral functions as corrected by phonon-phonon interactions.

What seems not to have been widely appreciated in the past about this methodology of phonon basis states is its remarkable similarity to the approach originated[21] by Feynman and Cohen and carried further[22] by Feenberg and co-workers in their study of the excitation spectrum of the superfluid phase of liquid He^4. Even though the mathemetical techniques were developed independently and to some extent concurrently, the recent literature does not indicate the close connections between the two programs. We will find here, by being able to pursue two distinct physical problems with what is essentially a single formalism, that we can enlarge our understanding of the formalism beyond that achieved so far within each problem separately.

II. HAMILTONIAN MATRIX

A. Basis States and Matrix Elements

The trial ground-state wave function, as a product of Jastrow and Gaussian factors, has already been exhibited in Eqs. (1.1) and (1.2). In order to display the excited states, we first introduce a diagonal representation for the displacement correlation function,

$$\overleftrightarrow{D}_{ij}=\textstyle\sum_\Lambda D_\Lambda(M_i M_j)^{-1/2}\vec{\epsilon}^{\,i}_\Lambda\epsilon^{j*}_\Lambda\ , \qquad (2.1)$$

where the eigenvectors $\vec{\epsilon}^{\,i}_\Lambda$ are labeled by an index $\Lambda=1,\ldots,3N$ and obey the orthonormality and completeness relations

$$\textstyle\sum_i \vec{\epsilon}^{\,i*}_\Lambda\cdot\vec{\epsilon}^{\,i}_{\Lambda'}=\delta_{\Lambda,\Lambda'}\ ,\quad \sum_\Lambda \vec{\epsilon}^{\,i}_\Lambda\vec{\epsilon}^{\,j*}_\Lambda=\overleftrightarrow{1}\,\delta_{i,j}\ . \qquad (2.2)$$

Because $\overleftrightarrow{D}_{ij}$ is a symmetric matrix from its definition Eq. (1.8) there is a degeneracy in the phonon representation: If $\vec{\epsilon}^{\,i}_\Lambda$ is an eigenvector, then the vector labeled by Λ^* such that $\vec{\epsilon}^{\,i}_{\Lambda^*}=\vec{\epsilon}^{\,i*}_\Lambda$ is also an eigenvector with identical eigenvalue, $D_{\Lambda^*}=D_\Lambda$.

We then define displacement coefficients for individual phonon modes,

$$u_\Lambda\equiv\textstyle\sum_i M_i^{1/2}\,\vec{\epsilon}^{\,i*}_\Lambda\cdot\vec{u}_i\ . \qquad (2.3)$$

The excited states are expressed as polynomials in the u_Λ's acting on the ground state, where the coefficients are chosen to make the states mutally orthonormal. In terms of the nonorthonormal set

$$|\Lambda)\equiv u_\Lambda|0\rangle\ ,\quad |\Lambda_1,\Lambda_2)\equiv u_{\Lambda_1}u_{\Lambda_2}|0\rangle,\quad \text{etc.},\qquad (2.4)$$

the orthonormal set $|\Lambda_1,\ldots,\Lambda_n\rangle$ can be expressed by the linear combinations

$$|\Lambda_1,\ldots,\Lambda_n\rangle=\sum_{m=0}^{N}\ \sum_{\Lambda'_1,\ldots,\Lambda'_m}\alpha(\Lambda_1,\ldots,\Lambda_n;\ \Lambda'_1,\ldots,\Lambda'_m)|\Lambda'_1,\ldots,\Lambda'_m)\ . \qquad (2.5)$$

Matrix elements of the Hamiltonian in this basis set can be evaluated with the aid of the identity

$$\begin{aligned}\langle 0|P_n\mathcal{H}P_m|0\rangle={}&\langle 0|P_nP_m[\mathcal{V}-\textstyle\sum_i(\hbar^2/8M_i)\nabla_i^2\ln|\Psi_0|^2]|0\rangle\\&-\langle 0|\textstyle\sum_i(\hbar^2/8M_i)[P_n\nabla_i^2P_m+P_m\nabla_i^2P_n-2(\nabla_iP_n)\cdot(\nabla_iP_m)]|0\rangle\ ,\end{aligned}\qquad (2.6)$$

where $P_n=P_n(\{u_\Lambda\})$ is an nth-degree polynomial in the mode coordinates u_Λ. Inserting the expression (1.1) for Ψ_0 gives

$$\begin{aligned}\langle 0|P_n\mathcal{H}P_m|0\rangle={}&\langle 0|P_nP_m\mathcal{V}^*|0\rangle+\sum_{i<j}(\hbar^2/4M_{ij})\overleftrightarrow{\Gamma}_{ij}:\overleftrightarrow{1}\langle 0|P_nP_m|0\rangle\\&-\langle 0|\sum_i(\hbar^2/8M_i)[P_n\nabla_i^2P_m+P_m\nabla_i^2P_n-2(\nabla_iP_n)\cdot(\nabla_iP_m)]|0\rangle\ ,\end{aligned}\qquad (2.7)$$

where

$$\begin{aligned}\mathcal{V}^*&\equiv\sum_{i<j}v^*_{ij}(\vec{r}_{ij})\\&\equiv\sum_{i<j}[v_{ij}(\vec{r}_{ij})-(\hbar^2/4M_{ij})\nabla^2_{ij}\ln f^2_{ij}(\vec{r}_{ij})]\end{aligned}\qquad (2.8)$$

and where

$$M_{ij}\equiv[\tfrac{1}{2}(M_i^{-1}+M_j^{-1})]^{-1}\qquad (2.9)$$

is an average mass for the pair of particles. By utilizing the expression (2.7), one can write down various matrix elements; those of most immediate interest are

$$E_0=\langle 0|\mathcal{V}^*|0\rangle+\sum_{i<j}(\hbar^2/4M_{ij})\overleftrightarrow{\Gamma}_{ij}:\overleftrightarrow{1}\ ,\qquad (2.10)$$

$$\langle 0|\mathcal{H}|\Lambda\rangle=D_\Lambda^{-1/2}\langle 0|u_\Lambda\mathcal{V}^*|0\rangle=0\ ,\qquad (2.11)$$

$$\langle 0|\mathcal{H}|\Lambda_1,\Lambda_2\rangle=\sum_{\Lambda,\Lambda'}\alpha(\Lambda_1,\Lambda_2;\Lambda,\Lambda')\times\langle 0|[u_\Lambda u_{\Lambda'}-\delta_{\Lambda^*,\Lambda'}D_\Lambda]\mathcal{V}^*|0\rangle-\tfrac{1}{4}\hbar^2\delta_{\Lambda^*,\Lambda'}\,, \qquad (2.12)$$

$$\langle\Lambda|\mathcal{H}|\Lambda'\rangle=(D_\Lambda D_{\Lambda'})^{-1/2}[\langle 0|u^*_\Lambda u_{\Lambda'}\mathcal{V}^*|0\rangle+\tfrac{1}{4}\hbar^2\delta_{\Lambda,\Lambda'}]+\sum_{i<j}(\hbar^2/4M_{ij})\overleftrightarrow{\Gamma}_{ij}:\overleftrightarrow{1}\,\delta_{\Lambda,\Lambda'}. \qquad (2.13)$$

B. Optimization of Basis States

The coefficients $\overleftrightarrow{\Gamma}_{ij}$ in the ground-state wave functions remain at our disposal. These may be chosen either variationally, to minimize the ground-state energy expectation value, or through the requirement that matrix elements between ground state and all two-phonon states vanish. As pointed out by Koehler, these conditions are in fact identical. Varying E_0 with respect to $\overleftrightarrow{\Gamma}_{ij}$, or more conveniently, with respect to the linear combinations

$$\overleftrightarrow{G}_{ij}=\sum_{i',j'}\tfrac{1}{2}(\delta_{i,i'}-\delta_{i,j'})(\delta_{i,j'}-\delta_{j,j'})\overleftrightarrow{\Gamma}_{i',j'} \qquad (2.14)$$

leads to

$$0=\delta E_0/\delta\overleftrightarrow{G}_{ij}=-\langle 0|(\vec{u}_i\vec{u}_j-\langle 0|\vec{u}_i\vec{u}_j|0\rangle)\mathcal{V}^*|0\rangle+(\hbar^2/4M_i)\delta_{i,j}\overleftrightarrow{1}\,. \qquad (2.15)$$

Comparing Eq. (2.15) with Eq. (2.12) via the transformation (2.3) shows that an entirely equivalent condition is

$$\langle 0|\mathcal{H}|\Lambda,\Lambda'\rangle=0 \qquad (2.16)$$

for all Λ, Λ'. When Eq. (2.16) is satisfied, the one-phonon matrix elements reduce simply to

$$\langle\Lambda|(\mathcal{H}-E_0)|\Lambda'\rangle=\delta_{\Lambda,\Lambda'}(\hbar^2/2D_\Lambda)\equiv\delta_{\Lambda,\Lambda'}\hbar\omega_\Lambda\,, \qquad (2.17)$$

where the second line provides a definition of the excitation frequency ω_Λ. The important implication is that the proper choice of $\overleftrightarrow{\Gamma}_{ij}$ not only removes all elements $\langle 0|\mathcal{H}|\Lambda,\Lambda'\rangle$ from the Hamiltonian matrix, but also diagonalizes the submatrix $\langle\Lambda|\mathcal{H}|\Lambda'\rangle$ and leads to one-phonon energies which are just given by the inverse eigenvalues of the displacement correlation.

Equation (2.15) can be rearranged into a more useful form by explicitly recognizing the product character of the ground-state wave function Eq. (1.1). Integrating the $\vec{u}_i\vec{u}_j$ factors by parts against the Gaussian factor (see Appendix A for details) gives

$$(\hbar^2/4M_i)\delta_{i,j}\,\overleftrightarrow{1}=\sum_{i',j'}\overleftrightarrow{G}^{-1}_{ii'}\cdot\overleftrightarrow{\Phi}_{i'j'}\cdot\overleftrightarrow{G}^{-1}_{j'j}\,, \qquad (2.18)$$

where we define

$$\overleftrightarrow{\Phi}_{ij}\equiv\langle\nabla_i\nabla_j[|\tilde{\Psi}|^2(v^*-\langle 0|v^*|0\rangle)]\rangle_G/\langle|\tilde{\Psi}|^2\rangle_G \qquad (2.19)$$

and use the notation that for any function $W=W(\vec{r}_1,\ldots,\vec{r}_N)$,

$$\langle W\rangle_G\equiv\int d^{3N}r\,\exp\left(-\frac{1}{2}\sum_{i,j}\vec{u}_i\cdot\overleftrightarrow{G}_{ij}\cdot\vec{u}_j\right)W(\vec{r}_1,\ldots,\vec{r}_N)\bigg/\int d^{3N}r\,\exp\left(-\frac{1}{2}\sum_{i,j}\vec{u}_i\cdot\overleftrightarrow{G}_{ij}\cdot\vec{u}_j\right). \qquad (2.20)$$

Equation (2.18) implies that if we diagonalize the "effective dynamical matrix" $\overleftrightarrow{\Phi}_{ij}$ so that

$$\overleftrightarrow{\Phi}_{ij}=(M_iM_j)^{1/2}\textstyle\sum_\Lambda\Omega^2_\Lambda\vec{e}^{\,i}_\Lambda\vec{e}^{\,j*}_\Lambda\,, \qquad (2.21)$$

with eigenvectors $\vec{e}^{\,i}_\Lambda$ which satisfy orthonormality and completeness conditions of the same form as (2.2) for the $\vec{\epsilon}^{\,i}_\Lambda$, then the $\overleftrightarrow{G}_{ij}$ are also diagonalized,

$$\overleftrightarrow{G}_{ij}=\textstyle\sum_\Lambda[\hbar/2(M_iM_j)^{1/2}\Omega_\Lambda]^{-1}\vec{e}^{\,i}_\Lambda\vec{e}^{\,j*}_\Lambda\,. \qquad (2.22)$$

The eigenvectors and eigenvalues of $\overleftrightarrow{\Phi}_{ij}$, however, are not the same as those of $\overleftrightarrow{D}_{ij}$. An evaluation of Eq. (1.8) similar to that of Appendix A yields

$$\overleftrightarrow{D}_{ij}=\overleftrightarrow{G}^{-1}_{ij}+\sum_{i',j'}\overleftrightarrow{G}^{-1}_{ii'}\cdot(\langle\nabla_{i'}\nabla_{j'}|\tilde{\Psi}|^2\rangle_G/\langle|\tilde{\Psi}|^2\rangle_G)\cdot\overleftrightarrow{G}^{-1}_{j'j}\,. \qquad (2.23)$$

Thus the self-consistently determined frequency Ω_Λ does not equal the phonon excitation frequency ω_Λ, even though they would be identical in the absence of short-range correlations.

While the formulas obtained thus far are algebraically rigorous, the presence of the factors $|\tilde{\Psi}|^2$, dependent on all $3N$ coordinates, is a fatal complication. Approximations must be introduced to reduce the formulas to a manageable level. The approximation generally used is the first-order van Kampen–Nosanow[19] cluster expansion on the ground-state energy E_0. For present purposes, however, we choose to describe it equivalently as an approximation on the two-body distribution function, which we define as

$$g_{ij}(\vec{r})\equiv\langle 0|\delta^3(\vec{r}-\vec{r}_{ij})|0\rangle. \qquad (2.24)$$

In terms of $g_{ij}(\vec{r})$, E_0 is rewritten as

$$E_0=\sum_{i<j}[(\hbar^2/4M_{ij})\overleftrightarrow{\Gamma}_{ij}:\overleftrightarrow{1}+\int d^3r\,g_{ij}(\vec{r})v^*_{ij}(\vec{r})]. \qquad (2.25)$$

The simplest physically reasonable approximation that can be made for $g_{ij}(\vec{r})$, based on the Jastrow product form for $\tilde{\Psi}$, Eq. (1.2), is

$$g_{ij}(\vec{r}) \cong \exp(-\tfrac{1}{2}\vec{u}\cdot\overleftrightarrow{\gamma}_{ij}\cdot\vec{u})\tilde{f}^{\,2}_{ij}(\vec{r}) \Big/ \int d^3r\, \exp(-\tfrac{1}{2}\vec{u}\cdot\overleftrightarrow{\gamma}_{ij}\cdot\vec{u}), \quad (2.26)$$

where

$$\tilde{f}^{\,2}_{ij}(\vec{r}) \equiv f^{\,2}_{ij}(\vec{r}) \Big/ \frac{\int d^3r\, \exp(-\frac{1}{2}\vec{u}\cdot\overleftrightarrow{\gamma}_{ij}\cdot\vec{u}) f^{\,2}_{ij}(\vec{r})}{\int d^3r\, \exp(-\frac{1}{2}\vec{u}\cdot\overleftrightarrow{\gamma}_{ij}\cdot\vec{u})}$$

$$\equiv f^{\,2}_{ij}(\vec{r}) / \langle f^{\,2}_{ij}\rangle_\gamma \quad (2.27)$$

and where $\overleftrightarrow{\gamma}_{ij}$ is defined (see Appendix B) by its three-dimensional tensor inverse:

$$\overleftrightarrow{\gamma}^{-1}_{ij} = \sum_{i',j'} (\delta_{i',i} - \delta_{i',j})(\delta_{j',i} - \delta_{j',j})\overleftrightarrow{G}^{-1}_{i'j'}$$

$$= \sum_{\Lambda} (\hbar/2\Omega_\Lambda)\left(\sum_l (\delta_{l,i} - \delta_{l,j}) M_l^{-1/2}\vec{e}^{\,l}_\Lambda\right) \times \left(\sum_l (\delta_{l,i} - \delta_{l,j}) M_l^{-1/2}\vec{e}^{\,l\,*}_\Lambda\right). \quad (2.28)$$

With approximation (2.26) for $g_{ij}(\vec{r})$, the condition that E_0 be stationary remains Eq. (2.18), but definition (2.19) reduces to

$$\overleftrightarrow{\Phi}_{ij} \cong \sum_{i',j'} \tfrac{1}{2}(\delta_{i,i'} - \delta_{i,j'})(\delta_{j,i'} - \delta_{j,j'})\langle\nabla\nabla\tilde{v}_{i'j'}\rangle_\gamma, \quad (2.29)$$

where $\tilde{v}$ is an effective potential,

$$\tilde{v}_{ij}(\vec{r}) \equiv \tilde{f}^{\,2}_{ij}(\vec{r})\left[v^*_{ij}(\vec{r}) - \int d^3r\, g_{ij}(\vec{r}) v^*_{ij}(\vec{r})\right]. \quad (2.30)$$

Similarly, Eq. (2.23) for the displacement correlation reduces to

$$\overleftrightarrow{D}_{ij} \cong \overleftrightarrow{G}^{-1}_{ij} + \sum_{i',j'} \overleftrightarrow{G}^{-1}_{ii'} \cdot \sum_{l,l'} \tfrac{1}{2}(\delta_{i',l} - \delta_{i',l'})(\delta_{j',l} - \delta_{j',l'})\langle\nabla\nabla\tilde{f}^{\,2}_{ll'}\rangle_\gamma \cdot \overleftrightarrow{G}^{-1}_{j'j}. \quad (2.31)$$

C. Corrections to Phonon Excitation Energies

Although states with zero, one, and two phonons excited have been constructed [Eqs. (2.4) and (2.5)] not all matrix elements of $\mathcal{H}$ using these states have been exhibited yet. If we view these states as forming a subspace out of a complete Hilbert space of states, then the matrix of $\mathcal{H}$ in the subspace must also include the elements $\langle\Lambda|\mathcal{H}|\Lambda_1, \Lambda_2\rangle$ and $\langle\Lambda_1, \Lambda_2|\mathcal{H}|\Lambda_1', \Lambda_2'\rangle$. The first of these is fairly simple to evaluate using identity (2.7) and the techniques of Appendix A:

$$\langle\Lambda|\mathcal{H}|\Lambda_1, \Lambda_2\rangle = D_\Lambda^{-1/2} \sum_{\Lambda',\Lambda''} \alpha(\Lambda_1, \Lambda_2; \Lambda', \Lambda'')\left\langle\left[\prod_\mu\left(\sum_{i,j} M_i^{1/2}\vec{\epsilon}^{\,i}_\mu\cdot\overleftrightarrow{G}^{-1}_{ij}\cdot\nabla_j\right)\right]\left[|\tilde{\Psi}|^2(\mathcal{V}^* - \langle 0|\mathcal{V}^*|0\rangle)\right]\right\rangle_G \Big/ \langle|\tilde{\Psi}|^2\rangle_G, \quad (2.32)$$

where the product runs over the three values $\mu = \Lambda^*, \Lambda'$, and Λ''. The remaining matrix elements, between pairs of two-phonon states, become quite lengthy when written out in generality. They simplify enormously if short-range correlations are entirely absent, in which case

$$\langle\Lambda_1, \Lambda_2|(\mathcal{H} - E_0)|\Lambda_1', \Lambda_2'\rangle_{f(r)\to 1}(\delta_{\Lambda_1,\Lambda_1'}\delta_{\Lambda_2,\Lambda_2'} + \delta_{\Lambda_1,\Lambda_2'}\delta_{\Lambda_2,\Lambda_1'})\hbar(\omega_{\Lambda_1} + \omega_{\Lambda_2})$$
$$+ \sum_{i<j}\left\langle\left\{\prod_\mu\left[\sum_l\left(\frac{\hbar}{2M_l\omega_\mu}\right)^{1/2}(\delta_{l,i} - \delta_{l,j})\vec{\epsilon}^{\,l*}_\mu\cdot\nabla\right]\right\} v_{ij}(\vec{r}_{ij})\right\rangle_\gamma, \quad (2.33)$$

where here μ takes on the four values $\mu = \Lambda_1', \Lambda_2', \Lambda_1^*$, and Λ_2^*. When short-range correlations are present, the formulas become complicated both because of the distinction between $\overleftrightarrow{G}^{-1}_{ij}$ and $\overleftrightarrow{D}_{ij}$ and because of the appearance of third and fourth derivatives of $|\tilde{\Psi}|^2$. Since we are ultimately interested in quantities which do not depend sensitively on two-phonon matrix elements, and since such elements are not numerically sensitive to these complications, we adopt the following approximation in the presence of short-range correlations:

$$\langle\Lambda_1, \Lambda_2|(\mathcal{H} - E_0)|\Lambda_1', \Lambda_2'\rangle \cong (\delta_{\Lambda_1,\Lambda_1'}\delta_{\Lambda_2,\Lambda_2'} + \delta_{\Lambda_1,\Lambda_2'}\delta_{\Lambda_2,\Lambda_1'})\hbar(\omega_{\Lambda_1} + \omega_{\Lambda_2})$$
$$+ \sum_{i<j}\left\langle\left\{\prod_\mu\left[\sum_l\left(\frac{\hbar}{2M_l\Omega_\mu}\right)^{1/2}(\delta_{l,i} - \delta_{l,j})\vec{\epsilon}^{\,l*}_\mu\cdot\nabla\right]\right\}\tilde{v}_{ij}(\vec{r}_{ij})\right\rangle_\gamma. \quad (2.34)$$

This also incorportates the approximation (2.26) for the two-body distribution function. Similar approximations for the matrix elements of Eq. (2.30) reduce them to

$$\langle\Lambda|\mathcal{H}|\Lambda', \Lambda''\rangle \cong D_\Lambda^{-1/2}\sum_{i<j}\left\langle\left\{\prod_\mu\left[\sum_l\left(\frac{\hbar}{2M_l\Omega_\mu}\right)^{1/2}(\delta_{l,i} - \delta_{l,j})\vec{\epsilon}^{\,l*}_\mu\cdot\nabla\right]\right\}\tilde{v}_{ij}(\vec{r}_{ij})\right\rangle_\gamma. \quad (2.35)$$

The approximation (2.26) on the two-body distribution function leading to Eqs. (2.34) and (2.35) is equivalent to a lowest-order van Kampen–Nosanow cluster expansion on excited-state as well as ground-state matrix elements.

The derivations of the one- and two-phonon matrix elements just presented have also implicitly used the E_0-minimization criterion (2.18). With this condition satisfied, so that $\langle 0|\mathcal{H}|\Lambda, \Lambda'\rangle = 0$, the full matrix of $\mathcal{H}$ in the zero-, one-, and two-phonon subspace is easily diagonalized. In particular, the lowest eigenvalue of this submatrix is just E_0 itself. Thus the condition (2.18) can also be viewed as a minimization of the lowest-energy eigenvalue in the zero-, one-, and two-phonon subspace, and not just in the zero-phonon subspace alone as implied by Eq. (2.15). Furthermore, the eigenvalues corresponding to one-phonon states have excitation energies corrected from the values $\hbar\omega_\Lambda$ by the inclusion of the off-diagonal elements $\langle \Lambda|\mathcal{H}|\Lambda', \Lambda''\rangle$. These improved phonon excitation energies are given by the roots of the secular equation

$$\det\left|(\hbar\omega_\Lambda-\lambda)\delta_{\Lambda,\Lambda'}-\sum_{\Lambda_1\leq\Lambda_2}\sum_{\Lambda_1'\leq\Lambda_2'}\langle\Lambda|\mathcal{H}|\Lambda_1,\Lambda_2\rangle\langle\Lambda_1,\Lambda_2|(\mathcal{H}-E_0-\lambda)|\Lambda_1',\Lambda_2'\rangle^{-1}\langle\Lambda_1',\Lambda_2'|\mathcal{H}|\Lambda'\rangle\right|=0, \qquad (2.36)$$

where the inverse is taken in the $3N(3N+1)/2$-dimensional product space indexed by the pair Λ_1, Λ_2.

In further evaluating this expression, attention must be given to the second line of Eq. (2.34), involving four derivatives of $\tilde{v}$. If this term were absent, Eq. (2.36) would simplify considerably to

$$\det\left|(\hbar\omega_\Lambda-\lambda)\delta_{\Lambda,\Lambda'}-\sum_{\Lambda_1\leq\Lambda_2}\langle\Lambda|\mathcal{H}|\Lambda_1,\Lambda_2\rangle(\hbar\omega_{\Lambda_1}+\hbar\omega_{\Lambda_2}-\lambda)^{-1}\langle\Lambda_1,\Lambda_2|\mathcal{H}|\Lambda'\rangle\right|=0. \qquad (2.37)$$

This is just the sort of second-order perturbation theory correction which intuition would anticipate. If atomic vibrational amplitudes were small so that all quantum crystal effects of both short-range and long-range character could be neglected, exactly the traditional cubic anharmonic second-order correction is recovered. The presence of the four-derivatives term in Eq. (2.34) is not unexpected, however, and can be understood on the basis of the self-consistent phonon theory where short-range correlations are neglected. It was first shown[23] by Götze and Michel that if elastic constants of a crystal are calculated in two ways, first, by twice differentiating the free energy with respect to strains and second, by taking the long-wavelength limit of the dynamical matrix, and if the energy is represented by the first-order self-consistent phonon approximation which is equivalent to Eq. (2.10), then the two calculations of the elastic constants agree provided the dynamical matrix includes the four-derivatives term. In the self-consistent phonon formalism, this term is due to the necessity of reminimizing E_0 with respect to $\overleftrightarrow{G}_{ij}$ for each differing set of strains, so that strain derivatives of E_0 implicitly involve strain derivatives of the two-particle distribution function. Although the derivation of Götze and Michel was only concerned with macroscopic elastic constants, it was assumed by Goldman *et al.* that inclusion of the four-derivatives term gives the proper phonon frequencies at all wavelengths. This hypothesis was confirmed[24] by Werthamer, who showed that the phonon frequencies observed in neutron scattering at low momentum transfers, when computed as the response of the first-order self-consistent phonon approximation at equilibrium to an externally applied disturbance, were given by the eigenvalues of Eq. (2.36) including the four-derivatives term.

III. COMPARISON WITH CORRELATED BASIS FUNCTION TREATMENT OF SUPERFLUID HELIUM

The theoretical approach to superfluid helium which was initiated originally[21] by Feynman and Cohen has subsequently been developed extensively[22] by Feenberg and co-workers and has been termed the "method of optimum correlated basis functions." It begins by making an explicit ansatz for the ground state of He II as a product wave function of the Jastrow form, with the pair function not further specified. It is then recognized that the low-lying excited states are related to density fluctuations with dispersion curve of the phonon-roton form, so that excited-state wave functions are constructed by multiplying low-order polynomials in the density operator into the ground state. Coefficients in the polynomials are determined so as to produce an orthonormal set of states, and matrix elements of the Hamiltonian are evaluated.

An optimization of the phonon basis set is next achieved by requiring the ground-state energy expectation to be a minimum, or equivalently by requiring the vanishing of all Hamiltonian matrix elements between states with n and $n \pm 2$ quanta of a particular phonon mode. The excitation spectrum is identified with the difference in energy expectations between the single phonon-roton state and the ground state. Further improvements on this description of the ground-state and phonon-roton excitation energies are achieved by taking account of additional off-diagonal matrix elements, although in the Feenberg scheme these are treated by perturbation theory and not by rediagonalization of sequentially enlarged finite submatrices.

The unperturbed phonon excitation spectrum in the Feenberg scheme is just the one originally obtained by Feynman,

$$\hbar\omega_k = \hbar^2 k^2 / 2MS(k), \tag{3.1}$$

where $S(k)$, the so-called liquid structure factor, is the Fourier transform of the two-body distribution function or equivalently of the density correlation function. Since the elementary excitations in the superfluid are density fluctuations, $S(k)$ can also be regarded as the phonon propagator and in that sense is the analog for the liquid of the displacement correlation $\overleftrightarrow{\mathrm{D}}$ in the solid. The Feynman formula, Eq. (3.1), is thus the formal analog of Eq. (2.17),

$$\hbar\omega_\Lambda = \hbar^2 / 2D_\Lambda\,. \tag{3.2}$$

Carrying the analogy further, Feenberg and coworkers have shown in detail that the first perturbation correction to the one-phonon excitations, involving the admixture with two-phonon states, produces a corrected excitation spectrum which agrees with that first proposed by Feynman and Cohen from consideration of the backflow of liquid around a moving localized disturbance. From this viewpoint, the classic three-phonon anharmonic process in a crystal is the formal analog of the Feynman-Cohen backflow effect in the superfluid liquid.[25]

When sketched in this way, the method of correlated basis functions is evidently identical in philosophy and procedure to that of Koehler. Some differences appear, however, upon closer inspection. In the first place, Feenberg is able to evaluate in a simple way matrix elements between states with rather large numbers of phonons because he restricts himself to long wavelengths, where interference terms analogous, for example, to the second term of Eq. (2.23) are negligible. In this way he is able to demonstrate that when E_0 is a minimum an entire infinite subset of off-diagonal matrix elements simultaneously vanishes. But such a result is really only valid for the acoustic-phonon part of the excitation spectrum, and extensions to the shorter-wavelength roton portion should be regarded as only of qualitative significance. As Koehler has demonstrated, the second term of Eq. (2.23), or more specifically of Eq. (2.31), is a correction substantially greater than 20% in solid helium near the Brillouin-zone boundary.

One aspect of the phonon-roton spectrum where this distinction could be critical is for the roton-roton resonance conjectured by Ruvalds and Zawadowski[26] and by Iwamoto and co-workers.[27] They were able to explain and predict a number of properties observed in neutron[28] and laser Raman-scattering[29] experiments on the basis of a strong interaction between two rotons, leading to a bound, or more likely a resonant, two-roton state. The theoretical analysis which Ruvalds and Zawadowski developed for this proposed effect follows the lines of earlier treatments[30] of possible two-phonon resonances observed[31] in SiO_2 and $AlPO_4$. In application to the latter crystalline cases, it is argued that such resonances reflect themselves in the near-vanishing of the two-phonon scattering probability, or in other words, in the existence of a nearly zero eigenvalue for the matrix $\langle \Lambda_1, \Lambda_2 | (\mathcal{H} - E_0 - \lambda) \times | \Lambda_1', \Lambda_2' \rangle$ which appears in Eq. (2.36). In this event, the phonon interaction represented by the off-diagonal second line of Eq. (2.34) is not at all negligible in comparison with the noninteracting phonon propagation represented by the first line. It is natural to extend this analytical approach to the superfluid liquid by employing the method of correlated basis functions, but with the crucial generalization of allowing for excitation interaction at short wavelengths in the evaluation of two-excitation matrix elements. Such a development would permit a quantitative first-principles investigation of whether two-roton resonances do indeed exist, given the actual microscopic parameters of liquid helium.

APPENDIX A

In this appendix we detail the transformation on the matrix element

$$\overleftrightarrow{\mathrm{K}}_{ij} \equiv \langle 0 | (\vec{\mathrm{u}}_i \vec{\mathrm{u}}_j - \langle 0 | \vec{\mathrm{u}}_i \vec{\mathrm{u}}_j | 0 \rangle) \mathcal{V}^* | 0 \rangle = \langle (\vec{\mathrm{u}}_i \vec{\mathrm{u}}_j - \langle 0 | \vec{\mathrm{u}}_i \vec{\mathrm{u}}_j | 0 \rangle) | \tilde{\Psi} |^2 \mathcal{V}^* \rangle_G / \langle | \tilde{\Psi} |^2 \rangle_G \tag{A1}$$

leading to Eq. (2.18). Recollecting definition (2.20), for any function $W = W(\vec{\mathrm{r}}_1, \ldots, \vec{\mathrm{r}}_N)$,

$$\langle W \rangle_G \equiv \int d^{3N} r \exp\left(-\frac{1}{2} \sum_{i,j} \vec{\mathrm{u}}_i \cdot \overleftrightarrow{\mathrm{G}}_{ij} \cdot \vec{\mathrm{u}}_j \right) W(\vec{\mathrm{r}}_1, \ldots, \vec{\mathrm{r}}_N) \Big/ \int d^{3N} r \exp\left(-\frac{1}{2} \sum_{i,j} \vec{\mathrm{u}}_i \cdot \overleftrightarrow{\mathrm{G}}_{ij} \cdot \vec{\mathrm{u}}_j \right). \tag{A2}$$

But by Taylor's theorem,

$$W(\vec{r}_1, \ldots, \vec{r}_N) = \exp(\textstyle\sum_l \vec{u}_l \cdot \nabla_l)\, W(\vec{R}_1, \ldots, \vec{R}_N), \tag{A3}$$

so that

$$\overleftrightarrow{K}_{ij} = \frac{\partial^2}{\partial \nabla_i\, \partial \nabla_j} \left\{ \left[\left\langle \exp\left(\sum_l \vec{u}_l \cdot \nabla_l\right)\right\rangle_G \left|\tilde{\Psi}\right|^2 \mathcal{V}^* \right] \Big/ \left[\left\langle \exp\left(\sum_l \vec{u}_l \cdot \nabla_l\right)\right\rangle_G \left|\tilde{\Psi}\right|^2 \right] \right\} . \tag{A4}$$

The Gaussian integrations are easily done by completing the square on the quadratic form in the exponent; then we have

$$\overleftrightarrow{K}_{ij} = \frac{\partial^2}{\partial \nabla_i\, \partial \nabla_j} \left\{ \left[\exp\left(\frac{1}{2} \sum_{i,j} \overleftrightarrow{G}^{-1}_{ij} : \nabla_i \nabla_j\right) \left|\tilde{\Psi}\right|^2 \mathcal{V}^* \right] \Big/ \left[\exp\left(\frac{1}{2} \sum_{i,j} \overleftrightarrow{G}^{-1}_{ij} : \nabla_i \nabla_j\right) \left|\tilde{\Psi}\right|^2 \right] \right\} , \tag{A5}$$

where $\overleftrightarrow{G}^{-1}_{ij}$ is an inverse in the $3N$-dimensional space such that

$$\textstyle\sum_l \overleftrightarrow{G}_{il} \cdot \overleftrightarrow{G}^{-1}_{lj} = \delta_{i,j} \overleftrightarrow{1} . \tag{A6}$$

Carrying out the differentiations gives

$$\overleftrightarrow{K}_{ij} = \sum_{i',j'} \overleftrightarrow{G}^{-1}_{ii'} \circ \exp\left(\frac{1}{2} \sum_{i,j} \overleftrightarrow{G}^{-1}_{ij} : \nabla_i \nabla_j\right) \nabla_{i'} \nabla_{j'} \left(\left|\tilde{\Psi}\right|^2 \left\{ \mathcal{V}^* - \left[\exp\left(\frac{1}{2} \sum_{i,j} \overleftrightarrow{G}^{-1}_{ij} : \nabla_i \nabla_j\right) \left|\tilde{\Psi}\right|^2 \mathcal{V}^* \right] \Big/ \left[\exp\left(\frac{1}{2} \sum_{i,j} \overleftrightarrow{G}^{-1}_{ij} : \nabla_i \nabla_j\right) \left|\tilde{\Psi}\right|^2 \right] \right\} \right) \cdot \overleftrightarrow{G}^{-1}_{j'j} \Big/ \left[\exp\left(\frac{1}{2} \sum_{i,j} \overleftrightarrow{G}^{-1}_{ij} : \nabla_i \nabla_j\right) \left|\tilde{\Psi}\right|^2 \right] . \tag{A7}$$

Reversing the steps which lead from Eq. (A1) to Eq. (A5) allows Eq. (A7) to be reexpressed as

$$\overleftrightarrow{K}_{ij} = (\langle |\Psi|^2 \rangle_G)^{-1} \sum_{i',j'} \overleftrightarrow{G}^{-1}_{ii'} \cdot \langle \nabla_{i'} \nabla_{j'} [|\tilde{\Psi}|^2 (\mathcal{V}^* - \langle 0|\mathcal{V}^*|0\rangle)] \rangle_G \cdot \overleftrightarrow{G}^{-1}_{j'j} , \tag{A8}$$

which is the same as Eqs. (2.18) and (2.19).

APPENDIX B

In this appendix we develop an expression for, and an approximation to, the two-body distribution function defined as in Eq. (2.24),

$$g_{ij}(\vec{r}) \equiv \langle \delta^3(\vec{r} - \vec{r}_{ij}) |\tilde{\Psi}|^2 \rangle_G / \langle |\tilde{\Psi}|^2 \rangle_G . \tag{B1}$$

Using the integral representation

$$\delta^3(\vec{r} - \vec{r}_{ij}) = (2\pi)^{-3} \int d^3k\, e^{i\vec{k}\cdot(\vec{r}_{ij} - \vec{r})} \tag{B2}$$

for the δ function, and using Eq. (1.2) together with Taylor's theorem on $|\tilde{\Psi}|^2$,

$$|\tilde{\Psi}(\vec{r}_1, \ldots, \vec{r}_N)|^2 = \left[\exp\left(\sum_{i<j} \vec{u}_{ij} \cdot \nabla_{ij}\right)\right] \prod_{i<j} f^2_{ij}(\vec{R}_{ij}) , \tag{B3}$$

leads to

$$g_{ij}(\vec{r}) = (2\pi)^{-3} \int d^3k \exp[-i\vec{k}\cdot(\vec{r} - \vec{R}_{ij})] \left[\left\langle \exp\left(i\vec{k} \cdot \vec{u}_{ij} + \sum_{i'<j'} \vec{u}_{i'j'} \cdot \nabla_{i'j'} \right) \right\rangle_G \left(\prod_{i'<j'} f^2_{i'j'}(\vec{R}_{i'j'}) \right) \right] \Big/ \left[\left\langle \exp\left(\sum_{i'<j'} \vec{u}_{i'j'} \cdot \nabla_{i'j'} \right) \right\rangle_G \left(\prod_{i'<j'} f^2_{i'j'}(\vec{R}_{i'j'}) \right) \right] . \tag{B4}$$

The techniques of Appendix A enable the Gaussian averages to be evaluated,

$$g_{ij}(\vec{r}) = (2\pi)^{-3} \int d^3k \exp[-i\vec{k}\cdot(\vec{r} - \vec{R}_{ij})] \left[\exp\left(-\tfrac{1}{2} \vec{k} \cdot \overleftrightarrow{d}_{ij,ij} \cdot \vec{k} + i\vec{k} \cdot \sum_{l<l'} \overleftrightarrow{d}_{ij,ll'} \circ \nabla_{ll'} \right) \right.$$
$$\left. \times \exp\left(\frac{1}{2} \sum_{i'<j'} \sum_{l<l'} \overleftrightarrow{d}_{i'j',ll'} : \nabla_{i'j'} \nabla_{ll'} \right) \left(\prod_{i'<j'} f^2_{i'j'}(\vec{R}_{i'j'}) \right) \right] \Big/ \left[\exp\left(\frac{1}{2} \sum_{i'<j'} \sum_{l<l'} \overleftrightarrow{d}_{i'j',ll'} : \nabla_{i'j'} \nabla_{ll'} \right) \left(\prod_{i'<j'} f^2_{i'j'}(\vec{R}_{i'j'}) \right) \right] , \tag{B5}$$

where

$$\overleftrightarrow{\mathrm{d}}_{ij,i'j'}=\langle\vec{\mathrm{u}}_{ij}\vec{\mathrm{u}}_{i'j'}\rangle_G=\sum_{l,l'}(\delta_{l,i}-\delta_{l,j})(\delta_{l',i'}-\delta_{l',j'})\overleftrightarrow{\mathrm{G}}^{-1}_{ll'}\ . \tag{B6}$$

The $\vec{k}$ integral can be carried out by completing the square of the quadratic form in the exponent:

$$g_{ij}(\vec{\mathrm{r}})=\left(\exp(-\tfrac{1}{2}\vec{\mathrm{u}}\cdot\overleftrightarrow{\gamma}_{ij}\circ\vec{\mathrm{u}})\bigg/\int d^3u\exp(-\tfrac{1}{2}\vec{\mathrm{u}}\cdot\overleftrightarrow{\gamma}_{ij}\cdot\vec{\mathrm{u}})\right)\left[\exp\left(\frac{1}{2}\sum_{i'<j'}\sum_{l<l'}(\overleftrightarrow{\mathrm{d}}_{i'j',ll'}-\overleftrightarrow{\mathrm{d}}_{i'j',ij}\cdot\overleftrightarrow{\gamma}_{ij}\cdot\overleftrightarrow{\mathrm{d}}_{ij,ll'}):\nabla_{i'j'}\nabla_{ll'}\right)\right.$$
$$\left.\times\exp\left(\vec{\mathrm{u}}\cdot\sum_{l<l'}\overleftrightarrow{\gamma}_{ij}\cdot\overleftrightarrow{\mathrm{d}}_{ij,ll'}\cdot\nabla_{ll'}\right)\left(\prod_{i'<j'}f^2_{i'j'}(\vec{\mathrm{R}}_{i'j'})\right)\right]\bigg/$$
$$\left[\exp\left(\frac{1}{2}\sum_{i'<j'}\sum_{l<l'}\overleftrightarrow{\mathrm{d}}_{i'j',ll'}:\nabla_{i'j'}\nabla_{ll'}\right)\left(\prod_{i'<j'}f^2_{i'j'}(\vec{\mathrm{R}}_{i'j'})\right)\right]\ , \tag{B7}$$

where $\overleftrightarrow{\gamma}_{ij}$ is the three-dimensional inverse of $\overleftrightarrow{\mathrm{d}}_{ij,ij}$,

$$\overleftrightarrow{\gamma}_{ij}\cdot\overleftrightarrow{\mathrm{d}}_{ij,ij}=\overleftrightarrow{1}. \tag{B8}$$

The factor occupying the first line of expression (B7) is simple enough to be retained in any approximation to $g_{ij}(\vec{\mathrm{r}})$. The remaining factors we approximate to lowest order by neglecting all terms containing $\overleftrightarrow{\mathrm{d}}_{i'j',ll'}$ with $i'j'\neq ll'$. Then

$$g_{ij}(\vec{\mathrm{r}})\cong[\exp(-\tfrac{1}{2}\vec{\mathrm{u}}\cdot\overleftrightarrow{\gamma}_{ij}\cdot\vec{\mathrm{u}})/\int d^3u\exp(-\tfrac{1}{2}\vec{\mathrm{u}}\cdot\overleftrightarrow{\gamma}_{ij}\cdot\vec{\mathrm{u}})]f^2_{ij}(\vec{\mathrm{r}})/[\exp(\tfrac{1}{2}\overleftrightarrow{\mathrm{d}}_{ij,ij}:\nabla_{ij}\nabla_{ij})f^2_{ij}(\vec{\mathrm{R}}_{ij})]$$
$$=[\exp(-\tfrac{1}{2}\vec{\mathrm{u}}\circ\overleftrightarrow{\gamma}_{ij}\cdot\vec{\mathrm{u}})f^2_{ij}(\vec{\mathrm{r}})]/[\int d^3r\exp(-\tfrac{1}{2}\vec{\mathrm{u}}\cdot\overleftrightarrow{\gamma}_{ij}\cdot\vec{\mathrm{u}})f^2_{ij}(\vec{\mathrm{r}})]\,. \tag{B9}$$

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Application of the Law of Corresponding States to Group-I and -II Metals[†]

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Reduced pressure, volume, and temperature variables $P^* = \sigma'^3 P/\epsilon'$, $V^* = V/N\sigma'^3$, and $T^* = kT/\epsilon'$, in which σ' is the atomic radius and ϵ' is the heat of sublimation per atom at 0 °K, are introduced as the basis for a new law of corresponding states. This law of corresponding states is applied to all experimental $P(T)$ vapor and sublimation pressure data for the group-I and -II elements. The $P^*(T^*)$ data for these elements fall on a common curve of the form $\ln P^* = a^* - b^*/T^*$, with an average deviation of about 40%, over ten decades in P^* from 10^{-15} to 10^{-5}. For group-II*b* elements alone the corresponding curve shows an average deviation of only 9.3% over almost seven decades in P^*. Expected extensions and limitations of this law of corresponding states are investigated. It is shown that the correspondence may extend to vapor- and sublimation-pressure curves of many substances over wide P and T ranges, but probably does not extend generally to other properties. This law of corresponding states is shown to have a theoretical basis in thermodynamics and the Clapeyron equation. Theoretical expressions for dP^*/dT^* and, approximately, for $P^*(T^*)$ are derived which show correspondence and agree with experiment. For the case of heavier rare gases, the present law of corresponding states is approximately identical to the usual law of corresponding states for van der Waals substances based on potential parameters. These two laws of corresponding states are compared.

I. INTRODUCTION

The law of corresponding states is an old law, originally formulated by van der Waals about 100 years ago.[1] A statement of the law of corresponding states which will be particularly useful to us is this: The equations of state of some substances may be written as a single universal equation of state in terms of suitable reduced variables. Thus, if the individual equations of state are $f_i(P, V, T) = 0$, then the universal equation of state is $F(P^*, V^*, T^*, \Lambda^*) = 0$. In these expressions P, V, and T are pressure, volume, and temperature; P^*, V^*, and T^* are the respective reduced variables, and Λ^* is a reduced quantum-mechanical parameter.

A characteristic part of the idea is the way in which properties are reduced, i.e., nondimensionalized. In this paper we shall be interested in a new way of reducing physical properties. In the earliest formulation of the law of corresponding states (LOCS), the quantities P, V, and T for a substance were reduced by dividing by the respective values at the critical point of the substance; i.e., the reduced variables were taken as $P_r = P/P_{\text{cr}}$, $V_r = V/V_{\text{cr}}$, and $T_r = T/T_{\text{cr}}$. The applications of the van der Waals LOCS all derive from the fact that the van der Waals equation of state may be written in a universal nondimensional form in terms of P_r, V_r, and T_r.[2]

The more modern form of the LOCS uses intermolecular potential parameters to form reduced variables from unreduced ones. Thus if ϵ and σ are, respectively, a characteristic intermolecular potential energy and distance, and m is the molecular mass, then the reduced pressure, volume, and temperature may be written as the nondimensional quantities

$$P^* = \sigma^3 P/\epsilon, \qquad V^* = V/N\sigma^3, \qquad T^* = kT/\epsilon . \qquad (1)$$

In Eq. (1), N is Avogadro's number and k is Boltzmann's constant. The quantum-mechanical parameter referred to above is $\Lambda^* = h/\sigma(m\epsilon)^{1/2}$, where h is Planck's constant.

The Schrödinger equation for N_0 particles interacting with a two-body potential $\epsilon f(r/\sigma)$ can be written in the universal nondimensional form[3-6]

$$\left[-\Lambda^{*2}\sum_i\left(\frac{1}{8\pi^2}\right)\nabla_i^{*2}+\sum_{i>k} f(r_{ik}^*) - NE_n^*\right] \times\Psi_n(\vec{r}_1^{\,*},\ldots,\vec{r}_{N_0}^{\,*}) = 0 . \qquad (2)$$