Self-Consistent Theory of Second-Order Elastic Constants with an Application to Noble-Gas Crystals

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Formal expressions for the first two strain derivatives of the first-order self-consistent free-energy density are rederived, and presented in a form suitable for numerical computation. The first strain derivative is the first-order self-consistent stress tensor and the second derivatives are the corresponding elastic constants. Because of the self-consistency condition, these elastic constants contain thermally averaged third- and fourth-order force constants. Special reference is made to an approximation first introduced by Horner in 1967. The expressions are applied to solid Ne, Ar, Kr, and Xe using a (12-6) Mie-Lennard-Jones potential. Calculations are carried out for the temperature range 0°K to their respective melting points at zero pressure. The calculations are presented for the 0°K volume, the experimental volume at zero pressure, and the volume produced by first-order self-consistent theory (SC). The volume effect is often large. However, at the *same volume*, the bulk moduli derived from F_{ISC} and F_{SC} differ by at most a few percent. This is taken to indicate the probable accuracy of our results.

I. INTRODUCTION

In a recent paper,[1] second-order elastic constants were calculated from the strain dependence of the quasiharmonic energy density. Numerical results were presented for noble-gas crystals. It was found that this work had certain unsatisfactory features that made a more complete theory desirable.

First, it turned out that the quasiharmonic free energy was not a reliable concept for Ne, except at absolute-zero temperature, because of large anharmonic effects. Second, a detailed study of the temperature dependence of the isothermal bulk modulus of Ar showed clearly that higher-order anharmonic effects cannot be ignored above about half the Debye temperature. By analogy, it was argued that this result applied to all the noble-gas crystals and to the separate elastic constants as well. Third, in our earlier work it was found that if the quasiharmonic approximation was used in the whole calculation, including the volume of the crystal, it provides a poor description of these solids. For all except the very lowest temperatures, the zero-pressure lattice constant was too large, and consequently quantities like the second-order elastic constants, which are very volume dependent, were much too small. This last problem was remedied, somewhat artificially, by calculating the elastic constants at the experimental volumes and at the 0°K volume. A fair description of the elastic constants of noble-gas solids was obtained in this way over a reasonable temperature range.

It is well known that the lowest-order self-consistent phonon theory[2] (SC) (based on first-order cumulants only) gives an improved description of the zero-pressure lattice constant compared to the quasiharmonic approximation. It seems natural, therefore, to examine elastic constants derived from an SC free energy.

The self-consistent theory of second-order elastic constants was first outlined by Choquard[3] through his general results for the first- and second-order thermodynamic derivatives of the free energy. A complementary theory using the functional derivative method was presented by Horner,[4] including a numerical application to He. This paper, however, contained an approximation which has generally been found to be unsatisfactory for the bulk modulus, and which we will examine here again for the individual elastic constants.

In a subsequent paper, Götze and Michel[5] generalized Choquard's and Horner's results to nonprimitive lattices and emphasized the importance of vertex renormalization effects on SC elastic constants. Finally, Werthamer[6] has rederived earlier SC elastic constants using a variational approach. None of these earlier papers, except Horner's, reported any numerical work.

It is the purpose of this paper, then, to present a calculation of the isothermal elastic constants of fcc Ne, Ar, Kr, and Xe based upon the lowest-order self-consistent free energy and a nearest-neighbor Lennard-Jones (12-6) potential. These elastic constants are the self-consistent generalizations of the quasiharmonic elastic constants referred to earlier. We emphasize that these elastic constants *explicitly* contain the effect of both cubic and quartic force constants.

Goldman et al.[7] have recently presented an improved self-consistent free energy (ISC) which contains the leading correction to SC. This theory gives a much better account of many thermodynamic properties of noble-gas crystals than does SC. Anticipating our results, we find that the elastic constants are very volume dependent. Nevertheless, we find that the SC bulk modulus and the one derived from the ISC free energy differ, at most, by a few percent *when calculated at the same volume*. We shall conclude (and extrapolate to all the second-order elastic constants) that although

ISC and SC elastic constants at their respective zero-pressure volumes are substantially different, this difference can be traced to the fact that the ISC free energy predicts a different crystal volume to the SC free energy. Since neither ISC or SC predicts reliable values for the zero-pressure lattice constant, and because of the strong volume dependence of the elastic constants, we decided to list isothermal elastic constants for Ne, Ar, Kr, and Xe evaluated at approximately the experimental zero-pressure crystal volume, and for clamped crystals at the $0°K$ volume, in Table III–V at the end of this paper. At these volumes, the ISC corrections are reasonably small for all temperatures.

The integral equations for the SC elastic constants are rederived in Sec. II using a space representation that is particularly useful for numerical work. The necessity of working with the full integral equation has recently been stressed by Klein et al.[8] in a study of the bulk moduli of Ar and Ne. The calculations are outlined in Sec. III. The various approximations to the complete SC elastic constants that have been proposed are discussed in Sec. IV. In Sec. V, we discuss our results at various volumes and make an estimate of higher-order contributions. Our paper should be regarded primarily as an investigation of the usefulness and range of validity of special dynamical models. Thus no attempt is made to confront our calculations with experiment.

II. ELASTIC CONSTANTS IN FIRST SELF-CONSISTENT APPROXIMATION

Elastic constants can be conveniently defined as suitable strain derivatives of a free-energy density. In this chapter, we chose the SC free energy and outline the analytical procedure for taking the required strain derivatives.

A. Self-Consistent Equations (SC1)

Following Choquard, let us introduce the first-order self-consistent equations

$$D_{\alpha\beta}(\mathbf{q}) = (2M)^{-1}\sum_\rho \eta_\rho(\mathbf{q})\eta_\rho^*(\mathbf{q}) \, \exp(\tfrac{1}{2}\lambda^\rho:\nabla\nabla)\varphi_{\alpha\beta}(\mathbf{R}_\rho),$$

where $\eta_\rho(\mathbf{q}) = \exp(i\mathbf{q}\cdot\mathbf{R}_\rho) - 1$, and

$$\lambda_{\alpha\beta}^\rho = (MN)^{-1}\sum_{\mathbf{q}j} \eta_\rho(\mathbf{q})\eta_\rho^*(\mathbf{q})$$
$$\times[\epsilon(\mathbf{q}j)/\omega_{\mathbf{q}j}^2]e_\alpha(\mathbf{q}j)e_\beta(\mathbf{q}j),$$

where $\epsilon(\mathbf{q}j) = \hbar\omega_{\mathbf{q}j}(n_{\mathbf{q}j}+\tfrac{1}{2})$. $\omega_{\mathbf{q}j}^2$ and $e_\alpha(\mathbf{q}j)$ are the eigenvalues and eigenvectors of $D_{\alpha\beta}(\mathbf{q})$, respectively. $n_{\mathbf{q}j} = [\exp(\hbar\omega_{\mathbf{q}j}/kT)-1]^{-1}$. The self-consistent Helmholtz free energy in first order then becomes

$$F = -\beta^{-1}\ln Z = -\tfrac{1}{2}N\sum_\rho \tfrac{1}{2}\lambda_{\alpha\beta}^\rho\Phi_{\beta\alpha}^\rho + \tfrac{1}{2}N\sum_\rho \Phi^\rho$$
$$+\beta^{-1}\sum_{\mathbf{q}j} \ln 2\sinh\tfrac{1}{2}\hbar\omega_{\mathbf{q}j}\beta. \quad (1)$$

Φ^ρ, Φ_α^ρ, $\Phi_{\alpha\beta}^\rho$, etc., are the smeared force constants

$$\exp(\tfrac{1}{2}\lambda^\rho:\nabla\nabla)\varphi(\mathbf{R}_\rho), \qquad \exp(\tfrac{1}{2}\lambda^\rho:\nabla\nabla)\varphi_\alpha(\mathbf{R}_\rho),$$
$$\exp(\tfrac{1}{2}\lambda^\rho:\nabla\nabla)\varphi_{\alpha\beta}(\mathbf{R}_\rho), \quad \text{etc.}$$

We also define

$$l_{\alpha\beta}(\mathbf{q}) = \sum_j e_\alpha(\mathbf{q}j)[\epsilon(\mathbf{q}j)/\omega_{\mathbf{q}j}^2]e_\beta(\mathbf{q}j),$$

in terms of which

$$\lambda_{\alpha\beta}^\rho = (MN)^{-1}\sum_{\mathbf{q}} \eta_\rho(\mathbf{q})\eta_\rho^*(\mathbf{q})l_{\alpha\beta}(\mathbf{q}).$$

Let us also note the convenient representation

$$l_{\alpha\beta}(\mathbf{q}) = \sum_\nu G_{\mathbf{q}\nu}{}^{\alpha\beta} = \sum_\nu [(2\pi\nu/\hbar\beta)^2+D_\mathbf{q}]^{-1}\beta^{-1}. \quad (2)$$

We further define $K = \tfrac{1}{2}N\sum_\rho \Phi^\rho$, and we note the useful relation

$$\partial K/\partial l_{\alpha\beta}(\mathbf{q}) = \tfrac{1}{2}D_{\alpha\beta}(\mathbf{q}). \quad (3)$$

B. First Derivatives of Free Energy

To obtain total derivatives (space) we shall assume the set $l_{\alpha\beta}(\mathbf{q})$ to be intermediate variables and then we shall use the chain rule. Thus consider a variable ε, which is a spacelike variable (i.e., it does not depend on temperature). Then

$$dF/d\varepsilon = (\partial F/\partial\varepsilon)_{\{l_{\alpha\beta}\}} + \sum_{\mathbf{q}}\sum_{\alpha\beta} [\partial F/\partial l_{\alpha\beta}(\mathbf{q})][dl_{\alpha\beta}(\mathbf{q})/d\varepsilon].$$

Using Eq. (1) for F, we obtain after much cancellation of terms (see Choquard[3])

$$dF/d\varepsilon = (\partial K/\partial\varepsilon)_{\{l_{\alpha\beta}(\mathbf{q})\}}.$$

This cancellation is due to the self-consistent condition imposed upon the frequencies and is peculiar to the first derivatives of the free energy. As we shall see, such simplification does not occur for higher derivatives.

C. Second Derivatives of Free Energy

Now we are concerned with

$$d^2F/d\varepsilon_2 d\varepsilon_1 = (d/d\varepsilon_2)(\partial K/\partial\varepsilon_1)_{\{l_{\alpha\beta}\}}$$
$$= \left(\frac{\partial^2 K}{\partial\varepsilon_2\partial\varepsilon_1}\right)_{\{l_{\alpha\beta}\}} + \sum_{\mathbf{q}\alpha\beta} \frac{\partial}{\partial l_{\alpha\beta}(\mathbf{q})}\frac{\partial K}{\partial\varepsilon_1}\frac{dl_{\alpha\beta}(\mathbf{q})}{d\varepsilon_2}$$
$$= \frac{\partial^2 K}{\partial\varepsilon_2\partial\varepsilon_1} + \sum_{\mathbf{q}\alpha\beta} \frac{\partial}{\partial\varepsilon_1}\frac{\partial K}{\partial l_{\alpha\beta}(\mathbf{q})}\frac{dl_{\alpha\beta}(\mathbf{q})}{d\varepsilon_2}.$$

Using Eq. (3), we obtain

$$d^2F/d\varepsilon_2 d\varepsilon_1 = \partial^2 K/\partial\varepsilon_2\partial\varepsilon_1 + \tfrac{1}{2}\sum_{\mathbf{q}\alpha\beta}(\partial D_q{}^{\alpha\beta}/\partial\varepsilon_1)[dl_{\alpha\beta}(\mathbf{q})/d\varepsilon_2].$$

Now with the help of Eq. (2) consider

$$dl_{\alpha\beta}(\mathbf{q})/d\varepsilon_2 = \sum_\nu (dG_{\mathbf{q}\nu}{}^{\alpha\beta}/d\varepsilon_2)$$
$$= \sum_\nu (-\beta)\sum_{\alpha'\beta'} G_{\mathbf{q}\nu}{}^{\alpha\alpha'}[dD_{\alpha'\beta'}(\mathbf{q})/d\varepsilon_2]G_{\mathbf{q}\nu}{}^{\beta\beta'}$$
$$= -\sum_{\alpha'\beta'}\sum_\nu \beta[G_{\mathbf{q}\nu}{}^{\alpha\alpha'}G_{\mathbf{q}\nu}{}^{\beta\beta'\dagger}][dD_{\alpha'\beta'}(\mathbf{q})/d\varepsilon_2]$$
$$= -\sum_{\alpha'\beta'} L_{\alpha\beta\alpha'\beta'}{}^{\mathbf{q}}[dD_{\alpha'\beta'}(\mathbf{q})/d\varepsilon_2],$$

where

$$L_{\alpha\beta\alpha'\beta'}{}^{q} = \beta \sum_{\nu} G_{q\nu}{}^{\alpha\alpha'} G_{q\nu}{}^{\beta\beta'\dagger}. \qquad (4)$$

Using Eq. (2) and the well-known method of summation (see, for instance, Morse and Feshbach[9]), one can show that

$$L_{\alpha\beta\alpha'\beta'}{}^{q} = \sum_{j_1 j_2} e_\alpha(\mathbf{q}j_1)e_\beta(\mathbf{q}j_2)e_{\alpha'}(\mathbf{q}j_1)e_{\beta'}(\mathbf{q}j_2)$$

$$\times \{\epsilon(\mathbf{q}j_1)/\omega_{qj_1}{}^2 - \epsilon(\mathbf{q}j_2)/\omega_{qj_2}{}^2\}(\omega_{qj_2}{}^2 - \omega_{qj_1}{}^2)^{-1}.$$

We shall also use the space representation of L,

$$L_{\alpha\beta\alpha'\beta'}{}^{p_1p_2} = (4M^2N)^{-1}$$

$$\times \sum_q L_{\alpha\beta\alpha'\beta'}{}^{q}\eta_{p_1}(\mathbf{q})\eta_{p_1}{}^*(\mathbf{q})\eta_{p_2}(\mathbf{q})\eta_{p_1}{}^*(\mathbf{q}).$$

Thus we can now write

$$d^2F/d\varepsilon_2 d\varepsilon_1 = \partial^2K/\partial\varepsilon_2\partial\varepsilon_1$$

$$-\tfrac{1}{2}\sum_q\sum_{\alpha\beta}\sum_{\alpha'\beta'}(\partial D_q{}^{\alpha\beta}/\partial\varepsilon_1)L_{\alpha\beta\alpha'\beta'}{}^{q}(dD_q{}^{\alpha'\beta'}/d\varepsilon_2).$$

If we go over to the space representation, we obtain by substituting the expression for $D_{\alpha\beta}(\mathbf{q})$

$$d^2F/d\varepsilon_2 d\varepsilon_1 = \partial^2K/\partial\varepsilon_1\partial\varepsilon_2$$

$$-\tfrac{1}{2}N\sum_{p_1p_2}\sum_{\alpha\beta\alpha'\beta'}(\partial\Phi_{\alpha\beta}{}^{p_1}/\partial\varepsilon_1)L_{\alpha\beta\alpha'\beta'}{}^{p_1p_2}(d\Phi_{\alpha'\beta'}{}^{p_2}/d\varepsilon_2). \quad (5)$$

The problem now is to find an expression for $d\Phi_{\alpha'\beta'}{}^{p_2}/d\varepsilon_2$:

$$d\Phi_{\alpha'\beta'}{}^{p_2}/d\varepsilon_2 = \partial\Phi_{\alpha\beta}{}^{p_2}/\partial\varepsilon_2$$

$$+ \sum_{q\gamma\delta}[\partial\Phi_{\alpha'\beta'}{}^{p_2}/\partial l_{\gamma\delta}(\mathbf{q})][dl_{\gamma\delta}(\mathbf{q})/d\varepsilon_2].$$

Going back to Eq. (4), we obtain

$$d\Phi_{\alpha'\beta'}{}^{p_2}/d\varepsilon_2 = \partial\Phi_{\alpha'\beta'}{}^{p_2}/\partial\varepsilon_2$$

$$- \sum_{q\gamma\delta}\sum_{\gamma'\delta'}[\partial\Phi_{\alpha'\beta'}{}^{p_2}/\partial l_{\gamma\delta}(\mathbf{q})]L_{\gamma\delta\gamma'\delta'}{}^{q}[dD_{\gamma'\delta'}(\mathbf{q})/d\varepsilon_2].$$

Now

$$\partial\Phi_{\alpha'\beta'}{}^{p_2}/\partial l_{\gamma\delta}(\mathbf{q}) = [\partial/\partial l_{\gamma\delta}(\mathbf{q})]\exp(\tfrac{1}{2}\lambda^{p_2}\!:\!\nabla\nabla)\varphi_{\alpha'\beta'}(\mathbf{R}_{p_2})$$

$$= (2MN)^{-1}\eta_{p_2}(\mathbf{q})\eta_{p_2}{}^*(\mathbf{q})\Phi_{\alpha'\beta'\gamma\delta}{}^{p_2}.$$
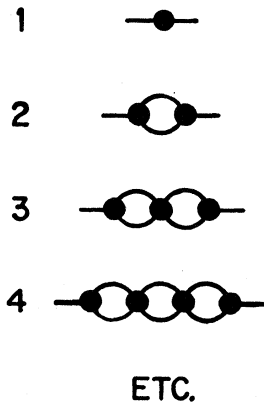

FIG. 1. Diagrammatic representation of Eq. (8). The first term corresponds to the frequencies occurring in Eq. (1). The second term was first discussed by Horner.

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TABLE I. Contributions to the elastic constant H_{11} (kbar) of successive terms illustrated in Fig. 1. The term labeled 1 corresponds to the first term on the right-hand side of Eq. (8). The terms labeled 2–15 are the successive terms obtained from the series expansion of $[1+C]^{-1}$. Horner's approximation neglected all terms beyond the second. All calculated elastic constants are given at the experimental volume.

Term	Neon 0°K	Neon 23.5°K	Xenon 0°K	Xenon 160°K
1	21.55	19.19	56.64	46.88
2	−7.20	−12.53	−1.88	−28.48
3	+2.10	+7.00	+0.05	+14.70
4	−0.63	−3.99		−7.74
5	+0.20	+2.29		+4.13
6	−0.06	−1.33		−2.22
7	+0.01	+0.78		+1.21
8		−0.46		−0.66
9		+0.27		+0.36
10		−0.16		−0.19
11		+0.10		+0.11
12		−0.06		−0.06
13		+0.03		+0.03
14		−0.02		−0.01
15		+0.01		
Total 2→15	−5.580	−8.072	−1.829	−18.815

Also

$$dD_{\gamma'\delta'}(\mathbf{q})/d\varepsilon_2 = (2M)^{-1}\sum_{p_3}\eta_{p_3}(\mathbf{q})\eta_{p_3}{}^*(\mathbf{q})(d\Phi_{\gamma'\delta'}{}^{p_3}/d\varepsilon_2).$$

Thus

$$d\Phi_{\alpha'\beta'}{}^{p_2}/d\varepsilon_2 = \partial\Phi_{\alpha'\beta'}{}^{p_2}/\partial\varepsilon_2$$

$$- \sum_{q\gamma\delta\gamma'\delta'}\sum_{p_3}(4M^2N)^{-1}\eta_{p_2}(\mathbf{q})\eta_{p_2}{}^*(\mathbf{q})$$

$$\times\Phi_{\alpha'\beta'\gamma\delta}{}^{p_2}\eta_{p_3}(\mathbf{q})\eta_{p_3}{}^*(\mathbf{q})(d\Phi_{\gamma'\delta'}{}^{p_3}/d\varepsilon_2)$$

or

$$d\Phi_{\alpha'\beta'}{}^{p_2}/d\varepsilon_2 = \partial\Phi_{\alpha'\beta'}{}^{p_2}/\partial\varepsilon_2$$

$$- \sum_{p_3\gamma\delta}\sum_{\gamma'\delta'}\Phi_{\alpha'\beta'\gamma\delta}{}^{p_2}L_{\gamma\delta\gamma'\delta'}{}^{p_2p_3}(d\Phi_{\gamma'\delta'}{}^{p_3}/d\varepsilon_2). \quad (6)$$

Equation (6) is an integral equation which could be solved by successive iteration.

It is useful now to symbolize the various tensor contractions by the symbol $\otimes$. Further, we define

$$C_{\alpha\beta\gamma\delta}{}^{p_1p_2} = \sum_{\gamma'\delta'}\Phi_{\alpha\beta\gamma'\delta'}{}^{p_1}L_{\gamma'\delta'\gamma\delta}{}^{p_1p_2}.$$

$\otimes$ is defined as a lattice sum and a sum over two Cartesian coordinates, so the Eq. (6) can be written

$$\frac{d\Phi_{\alpha'\beta'}{}^{p_2}}{d\varepsilon_2} = \frac{\partial\Phi_{\alpha'\beta'}{}^{p_2}}{\partial\varepsilon_2} - \left(C\otimes\frac{d\Phi}{d\varepsilon_2}\right)_{\alpha'\beta'}^{p_2}$$

or

$$d\Phi_{\alpha'\beta'}{}^{p_2}/d\varepsilon_2 = ([1+C]^{-1}\otimes\partial\Phi/\partial\varepsilon_2)_{\alpha'\beta'}{}^{p_2}$$

$$= ([1-C+C^2-C^3+\cdots]\otimes\partial\Phi/\partial\varepsilon_2)_{\alpha'\beta'}{}^{p_2}.$$

TABLE II. Sensitivity of the second term on the right-hand side of Eq. (8) to the number of q points used in the scan of the Brillouin zone for Ne at $0°K$.

No. of q points	H_{xxxx}	H_{xxyy}	H_{xyxy}
256	−5.587	−3.664	−2.542
2048	−5.580	−3.668	−2.536

Thus we have now our desired result:

$$d^2F/d\epsilon_2 d\epsilon_1 = \partial^2 K/\partial\epsilon_2\partial\epsilon_1$$
$$-\tfrac{1}{2}N \sum_{\rho 1\rho 2\rho 3} \sum_{\alpha\beta\alpha'\beta'\gamma\delta} (\partial\Phi_{\alpha\beta}{}^{\rho 1}/\partial\epsilon_1)L_{\alpha\beta\gamma\delta}{}^{\rho 1\rho 2}$$
$$\times[1+C]^{-1}{}_{\gamma\delta\alpha'\beta',}{}^{\rho 2\rho 3}(\partial\Phi_{\alpha'\beta',}{}^{\rho 3}/\partial\epsilon_2), \quad (6')$$

with

$$1_{\alpha\beta\gamma\delta}{}^{\rho 1\rho 2} = \delta_{\rho 1\rho 2}\delta_{\alpha\gamma}\delta_{\beta\delta}$$

and

$$C_{\alpha\beta\gamma\delta}{}^{\rho 1\rho 2} = \sum_{\mu\nu} \Phi_{\alpha\beta\mu\nu}{}^{\rho 1}L_{\mu\nu\gamma\delta}{}^{\rho 1\rho 2}.$$

D. Application to Elastic Constants

We define

$$H_{iklm} = (Nv)^{-1}(\partial^2F/\partial u_{ik}\partial u_{lm}), \quad (7)$$

where the u_{ij}'s are homogeneous strain parameters;

$$\partial/\partial u_{ik} = \sum_\rho \mathbf{R}_k{}^\rho(\partial/\partial\mathbf{R}_i{}^\rho).$$
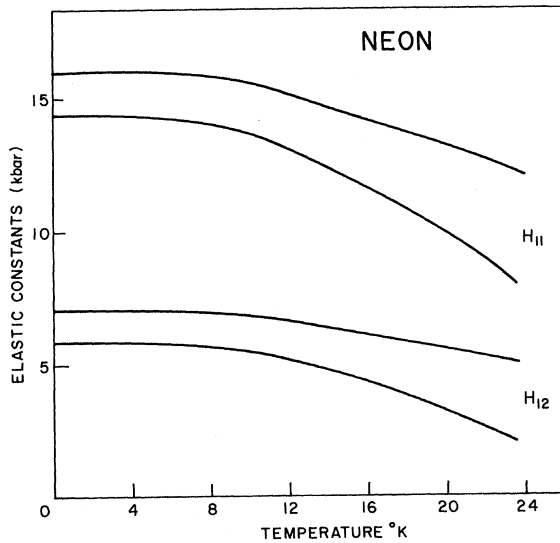
H_{iklm} are the elastic constants.

FIG. 2. Test of Horner's approximation for Ne. The upper curve corresponds to the complete evaluation of Eq. (8) (all the terms shown in Fig. 1). The lower curve corresponds to setting $C=0$ in Eq. (8) (the first two terms in Fig. 1). All results are for the volume for which $p_{SC}=0$.

Thus, if $\epsilon_1 \equiv u_{ik}$ and $\epsilon_2 \equiv u_{lm}$, we can use Eq. (6') immediately to obtain

$$d^2F/du_{ik}du_{lm} = \partial^2 K/\partial u_{ik}\partial u_{lm}$$
$$-\tfrac{1}{2}N \sum_{\rho 1\rho 2\rho 3;\ \alpha\beta\gamma\delta\gamma'\delta'} (\partial\Phi_{\alpha\beta}{}^{\rho 1}/\partial u_{ik})L_{\alpha\beta\gamma\delta}{}^{\rho 1\rho 2}$$
$$\times[1+C]^{-1}{}_{\gamma\delta\gamma'\delta',}{}^{\rho 2\rho 3}(\partial\Phi_{\gamma'\delta',}{}^{\rho 3}/\partial u_{lm}).$$

Substituting for $K = \tfrac{1}{2}N\sum_\rho\Phi^\rho$ and using Eq. (7), we obtain

$$NvH_{iklm} = \tfrac{1}{2}N \sum_\rho \mathbf{R}_k{}^\rho\mathbf{R}_m{}^\rho\Phi_{ik}{}^\rho$$
$$-\tfrac{1}{2}N \sum_{\rho 1\rho 2\rho 3;\ \alpha\beta\gamma\delta\gamma'\delta'} \mathbf{R}_k{}^{\rho 1}\Phi_{i\alpha\beta}{}^{\rho 1}L_{\alpha\beta\gamma\delta}{}^{\rho 1\rho 2}$$
$$\times[1+C]^{-1}{}_{\gamma\delta\gamma'\delta',}{}^{\rho 2\rho 3}\Phi_{\gamma'\delta' l}{}^{\rho 3}\mathbf{R}_m{}^{\rho 3}. \quad (8)$$
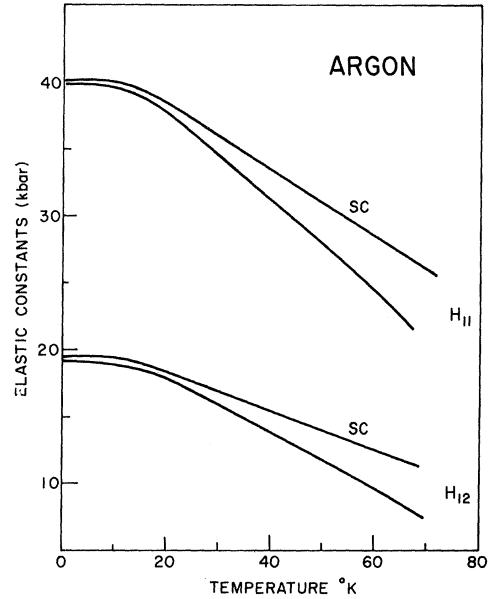

FIG. 3. Like Fig. 2 but for Ne→Ar.

The structure of Eq. (8) is illustrated in Fig. 1. The first diagram corresponds to the first term on the right-hand side of Eq. (8). Successive terms occurring in the expansion of the last term in Eq. (8) are illustrated in the remaining diagrams.

Before leaving the section, we recall that elastic constants as defined by Eq. (7) do not have the full symmetry properties of usual second-order elastic constants unless the solid is under zero stress, i.e.,

$$H_{ik} = (Nv)^{-1}(\partial F/\partial u_{ik}) = 0.$$

Strictly speaking, then, one *cannot* use Voigt's notation, $H_{xxxx} = H_{11}$, $H_{xxyy} = H_{12}$, and $H_{xyxy} = H_{44}$, since for example, in general, $H_{xyxy} \neq H_{xyyx}$. Nevertheless, for convenience, the above notation has been used in the figures for labeling the various curves.
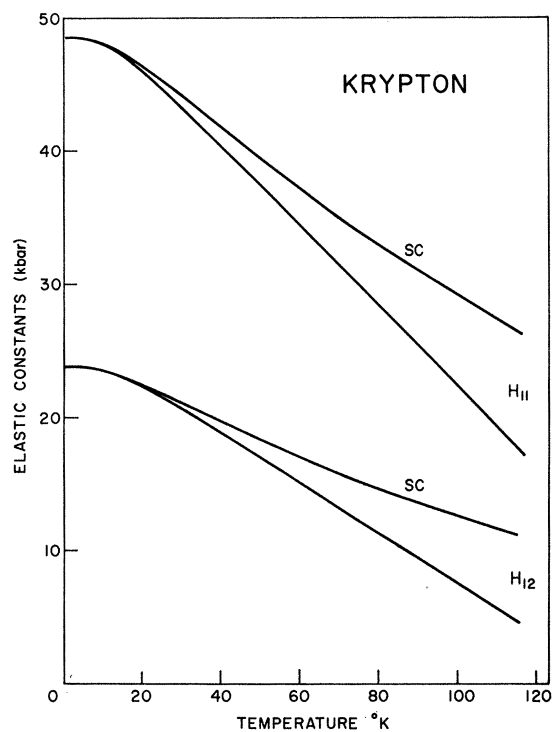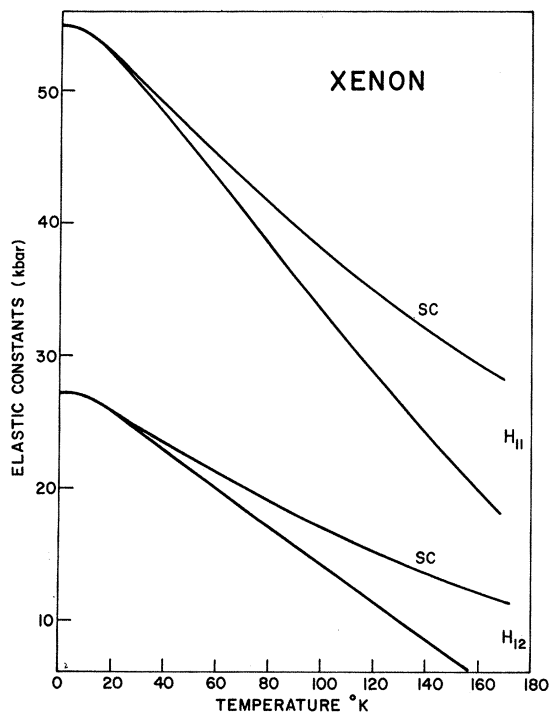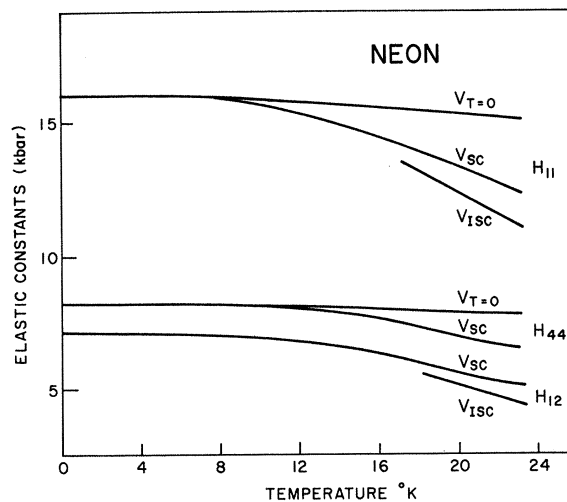
FIG. 4. Like Fig. 2 but for Ne→Kr.

FIG. 6. Illustration of the volume dependence of the elastic constants.

III. OUTLINE OF CALCULATIONS

All the calculations reported on in this paper have been carried out using a nearest-neighbor Mie-Lennard-Jones interatomic potential

$$\varphi(\mathbf{R}_p) = \varepsilon[(\mathbf{R}_0/\mathbf{R}_p)^{12} - 2(\mathbf{R}_0/\mathbf{R}_p)^6], \qquad (9)$$

where the parameters ε and R_0 have been taken from Horton's review article.[10] Near the origin Eq. (9) is cut off so that the smeared force constants derived from this potential [see expressions after Eq. (1)] are well behaved. We believe that our results are not significantly
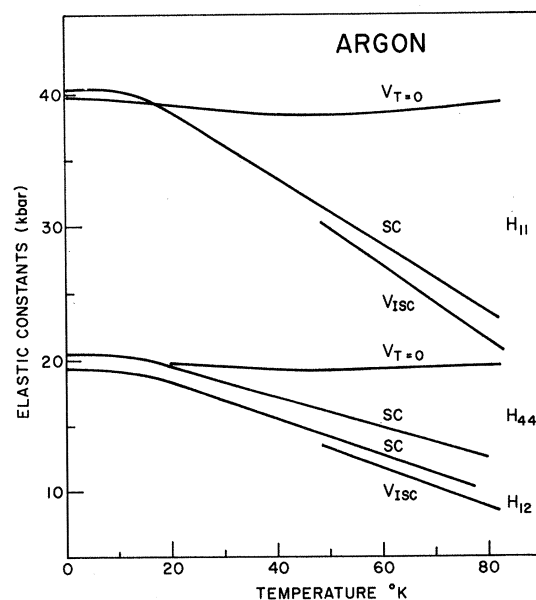

FIG. 5. Like Fig. 2 but for Ne→Xe.
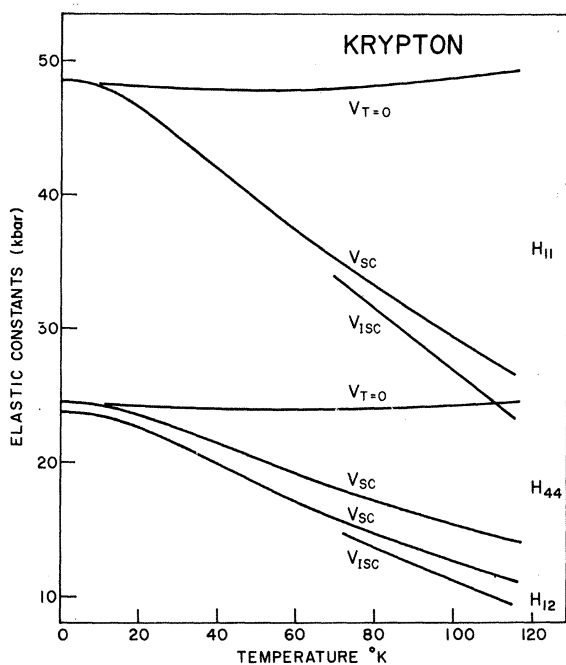

FIG. 7. See Fig. 6.

FIG. 8. See Fig. 6.

affected by this procedure. The arguments for this choice have been presented elsewhere.[11]

The method of solving the self-consistent equations for the frequencies and eigenvectors and the force constants, e.g., $\langle\varphi_{\alpha\beta\gamma}\rangle_{SC}$, has been discussed elsewhere.[7]
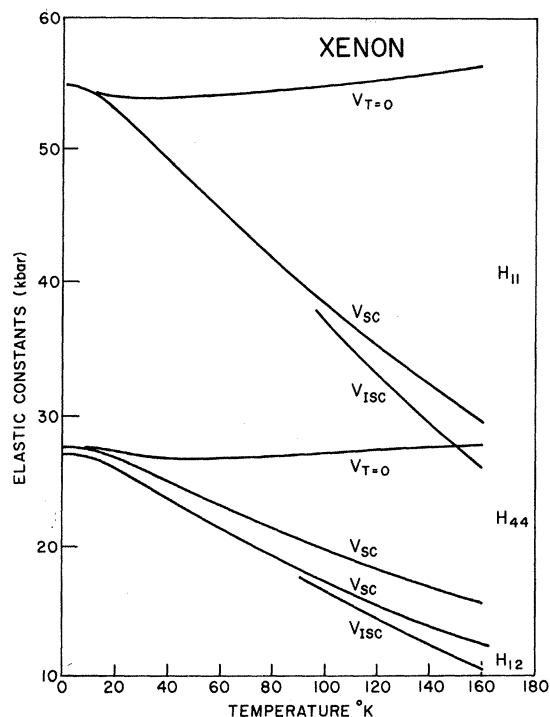

FIG. 9. See Fig. 6.

The only new feature of the present calculations is the explicit appearance of the fourth-order force constants.

The term involving $[1+C]^{-1}$ can be evaluated either by direct matrix inversion or by series expansion in powers of C. We have used both methods in the present paper.

The series expansion gives rise to the diagrammatic representation shown in Fig. 1 starting with the second diagram. Our isothermal elastic constants are directly related to the quasistatic limit of the phonon self-energy which is symbolically given in Fig. 1. We emphasize that the vertices are fully renormalized and that the lines are the first-order propagators. We stress that the evaluation of each diagram in the first figure involves only a single scan over the Brillouin zone, which was
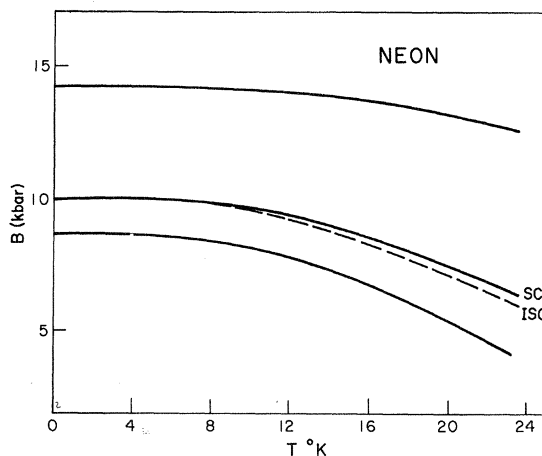

FIG. 10. Bulk modulus of Ne calculated in various approximations. The upper curve is derived from the frequencies occurring in Eq. (1). The curve labeled SC is calculated from Eq. (8) and the lowest one corresponds to Horner's approximation [$C=0$ in Eq. (8)]. The dashed curve is calculated from $(V\partial^2 F_{\rm ISC}/\partial V^2)_T$. All the curves have been calculated at the volume for which $P_{\rm ISC}=0$.

carried out using 2048 **q** points in the full zone. For selected points in reciprocal space we have also used 256 points in the full zone to check the accuracy of our results. The convergence of the self-energy is illustrated in Table I. We see that at most 15 terms are required for the heavier noble-gas solids. From Table II, we see that 2048 **q** points give adequate accuracy and selected results are contained in the figures.

IV. COMPARISON TO PREVIOUS WORK

Feldman et al.[1] have carried out calculations using the quasiharmonic free energy and the same interatomic potentials. They presented no result for Ne. The present isothermal constants agree quite well with theirs at low temperatures. At higher temperature our isothermal constants show a smaller temperature dependence. However, through a fortuitous cancellation, adiabatic

constants derived from both theories (at the experimental zero-pressure volumes) are very similar at all temperatures.

Gillis et al.[2] calculated wave velocities using the leading term only of Eq. (8). That this procedure does not give useful results was pointed out independently by Götze and Michel[5] and by Goldman et al.[7] Horner[4] truncated the series in Eq. (8) after the second term. The necessity of using the full series was first pointed

TABLE III. Elastic constants at approximately the zero-pressure volumes for various temperatures. Please note that $H_{xxxx} = c_{11}$, $H_{xxyy} = c_{11} - p$, and $H_{xyxy} = c_{44}$. Also note that p is the pressure in the SC approximation and the bulk modulus $B = -(V\partial p/\partial V)_T$. All quantities are in kbar except for the lattice parameter a in Å.

T	a	H_{xxxx}	H_{xxyy}	H_{xyxy}	B	p
			Neon			
0.00	4.4640	15.97	7.10	8.25	10.06	...
7.00	4.4646	15.88	7.05	8.21	9.99	−0.16
10.00	4.4677	15.52	6.87	8.04	9.75	−6.12
19.00	4.4983	12.96	5.49	6.84	7.95	−51.16
23.50	4.5187	11.12	4.50	5.97	6.65	−95.25
			Argon			
0.00	5.3111	39.78	19.16	20.12	26.00	−51.59
10.00	5.3117	39.58	19.05	20.03	25.87	−50.34
25.00	5.3235	36.91	17.50	18.77	23.95	−38.59
55.00	5.3801	29.24	13.04	15.16	18.41	−50.74
70.00	5.4209	25.19	10.78	13.24	15.52	−102.4
83.00	5.4259	21.47	8.76	11.48	12.88	−183.5
			Krypton			
0.00	5.6459	48.76	23.92	24.51	32.20	13.09
10.00	4.6469	48.40	23.70	24.34	31.95	13.59
25.00	5.6581	45.66	22.07	23.05	29.95	37.61
55.00	5.7003	38.85	18.06	19.87	25.04	55.90
85.00	5.7570	32.07	14.17	16.59	20.14	2.35
115.00	5.8331	25.00	10.31	13.31	15.12	−139.9
			Xenon			
0.00	6.1322	54.81	27.08	27.50	36.32	−5.55
20.00	6.1369	53.29	26.15	26.83	35.23	42.64
40.00	6.1545	49.86	24.06	25.17	32.72	88.26
80.00	6.2107	41.42	19.12	21.22	26.56	−8.02
120.00	6.2777	33.62	14.72	17.56	20.94	−123.5
160.00	6.3405	28.06	11.67	14.90	17.06	−116.26

out by Klein et al.[7] in a calculation of the compressibility of Ne and Ar. The present paper extends their work to the individual isothermal elastic constants. The effect of taking the full series in C is compared to retaining the first two terms only (Horner's approximation) in Figs. 2–5. We confirm that for Ne at all temperatures Horner's approximation is unreliable. While this approximation is clearly reasonable for Kr and Xe at low temperatures, it again breaks down at higher temperatures.
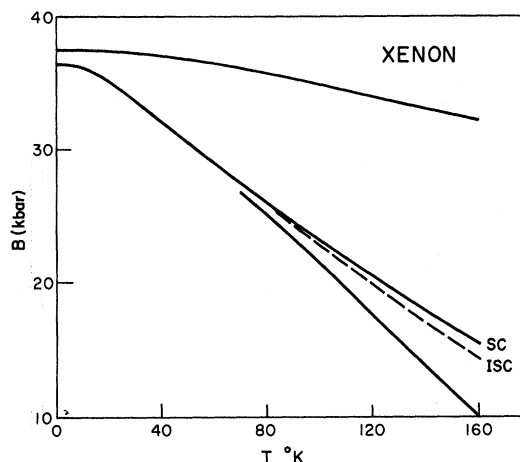

FIG. 11. Like Fig. 10 with Ne→Xe.

V. VOLUME DEPENDENCE AND HIGHER-ORDER EFFECTS

We have recently studied the thermodynamic properties of solid noble gases[7] in both the SC and ISC approximation. The SC approximation gives volumes that are significantly too low, while the ISC approxima-

TABLE IV. Temperature dependence of elastic constants of crystals clamped at approximately their 0°K volumes. Listed quantities are in kbar.

T	H_{xxxx} c_{11}	H_{xxyy} $c_{12} - p$	H_{xyxy} c_{44}	p
		Neon $a = 4.4640$ Å		
0	15.99	7.108	8.262	2.02
10	15.82	7.021	8.173	20.57
19	15.26	6.699	7.885	152.02
23	15.11	6.599	7.797	242.05
		Argon $a = 5.3111$ Å		
0	39.78	19.16	20.12	−51.6
20	39.07	18.73	19.77	+51.9
40	38.42	18.16	19.39	444.6
60	38.59	16.07	19.37	909.0
80	39.08	18.22	19.50	1376.5
		Krypton $a = 5.6459$ Å		
0	48.76	23.92	24.51	13.09
20	48.01	23.42	24.13	149.5
55	47.72	22.87	23.86	870.8
85	48.34	22.99	24.01	1517
115	49.20	23.32	24.28	2138
		Xenon $a = 6.1322$ Å		
0	54.81	27.08	27.50	−5.55
30	53.94	23.40	27.05	+284.7
80	54.27	26.14	27.03	1183
120	55.07	26.37	27.25	1877
160	56.02	26.73	27.55	2536

TABLE V. Some selected values of isothermal→adiabatic correction in the SC approximation.

T (°K)	a (Å)	$\gamma^2 TC_v/V$ (kbar)
	Neon	
19	4.502	0.96
23	4.529	1.28
	Argon	
60	5.400	3.50
80	5.464	4.04
	Krypton	
85	5.773	4.30
115	5.852	4.90
	Xenon	
120	6.283	4.73
160	6.364	5.35

tion predicts volumes that are somewhat too high. Figures 6–9 show how SC H's depend upon volume, and we see that this is substantial effect.

In this section we want to discuss how reliable our SC elastic constants are. That is, how big is the explicit effect of ΔF not included in F^{SC}? Since we have information on ISC elastic constants only for the bulk modulus, we will discuss this case now. We show the SC and ISC bulk moduli in Figs. 10 and 11 for Ne and Xe at the ISC volumes predicted by the respective approximations. It is clear that the results are rather close, even at high temperature. We conclude that (i) the bulk modulus is substantially volume dependent and (ii) the difference between the SC and ISC bulk moduli is largely due to the failure of the SC model to predict the volume of the crystal properly. We have seen this directly by noting that the ISC contribution to the first volume derivative is much larger than the

corresponding contribution to the second derivative. We will assume that the conclusions drawn from the bulk molduli apply equally to the other elastic constants. Thus, we believe that our SC elastic constants are reliable to $\sim7\%$ or so as long as they are calculated at the proper volume. For comparison with experimentally measured elastic constants—not a primary concern of this paper—we have listed in Tables II and III elastic SC constants calculated at the experimental volume of the crystal.

Since experiments have been reported on clamped crystals and others are in progress, we also present SC elastic constants at the 0°K volume of the crystal (see Figs. 6 and 7 and Tables IV and V). We see that these are essentially independent of temperature.

VI. CONCLUSION

We have presented values of the self-consistent isothermal elastic constants for solid noble gas as a function of the volume and temperature. Our work is based on the (12-6) Lennard-Jones potential with nearest-neighbor forces. We show that SC elastic constants are likely to differ little from ISC elastic constants as long as they are both calculated at the same volume. We show that vertex renormalization effects are very large, and so Horner's approximation is not generally satisfactory for solid noble gases. We will present elsewhere a comparison of our work based on the self-consistent phonon theory with recent work employing Monte Carlo calculations[12] on classical systems of small numbers of particles.

ACKNOWLEDGMENTS

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