# Anharmonic Self-Consistent Theory of Crystals. II. The 2d and 3d Quartic Crystal Models

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In this paper we apply the method developed in part I for describing the crystalline state of two and three dimensional inert gases. For strong anharmonicity of fourth order, the equations of state of these gases are obtained. This way we calculate the thermoelastic properties of two and three dimensional argon, krypton and xenon using the Lennard-Jones potential. The corrections to the Helmholtz free energy and thermodynamic properties due to quantum effects are considered. The results are compared with the available experimental data.

*Key words:* Inert gases; Anharmonicity; Thermodynamic properties; Two- and three-dimensional crystals.

## I. Introduction

In solids, the deviations of atoms from their equilibrium sites are small compared to the interatomic distances up to the melting points. This enables the potential energy of a crystal lattice to be expanded in a Taylor series in powers of the atomic displacements. When we restrict ourself to the second term (harmonic or quasi-harmonic approximation), exact calculations of the statistical integrals of a crystal can be made [1–3]. On the other hand, the anharmonic effects in crystals become large when the temperature exceeds about half of the melting temperature [4]. So, they should be taken into consideration.

In part I of this work, anharmonic crystals have been described by one-particle functions obeying the equations derived from the Liouville equation for the N-particle probability density, which is not symmetric with respect to the interchange of the phase-space coordinates of two similar particles.

The aim of the present part II is to apply the method to two and three dimensional monoatomic systems. We investigate the anharmonic perfect three-dimensional crystal having a cubic lattice and perfect two-dimensional crystals with a hexagonal structure. The corrections due to quantum effects are considered to improve the calculation. The amplitudes of the atomic vibrations about lattice sites are obtained for an interaction potential including fourth order terms. We calculate the thermodynamic properties of two- and three-dimensional Ar, Kr, and Xe.

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## II. The 3D Quartic Self-Consistent Potential

Let us expand the self-consistent potential (see (5) in the part I) up to the fifth order:

$$u(\boldsymbol{q}) = u_0 + \sum_{l+m+n=1}^{5} F_{x^l y^m z^n} \frac{q_k^l q_y^m q_z^n}{l!\, m!\, n!} \tag{1}$$

with

$$F_{x^l y^m z^n} = \sum_{i+j+k=0}^{5-l-m-n} K_{x^{i+l} y^{j+m} z^{n+k}} \frac{(-1)^{i+j+k} \langle q_x^i q_y^j q_z^k \rangle}{i!\, j!\, k!}, \tag{2}$$

$$\langle q_x^i q_y^j q_z^k \rangle = \int q_x^i q_y^j q_z^k w(\boldsymbol{q})\, \mathrm{d}\boldsymbol{q}, \tag{3}$$

$$K_{x^i y^j z^k} = \frac{\partial^{i+j+k} K(q)}{\partial q_x^i \partial q_y^j \partial q_z^k}, \tag{4}$$

$$K(\boldsymbol{q} - \boldsymbol{q}') = \sum_{\boldsymbol{n} \neq 0} \Phi(\boldsymbol{q} - \boldsymbol{q}' - A\boldsymbol{n}), \tag{5}$$

where $\boldsymbol{q}$ and $\boldsymbol{q}'$ are the displacements of atoms from their lattice points, $A$ is the lattice matrix and $\boldsymbol{n}$ is a vector having integer components. The constants $K_{x^i y^j z^k}$ (versus $q$, but functions of the lattice parameter $a$) are non-zero only for even $(i + j + k)$, if the interac-

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tion $\Phi$ depends only upon the absolute value of $r$ (isotropic interaction).

For crystals possessing three symmetry planes $X=0$, $Y=0$ and $Z=0$, (1) can be written as

$$u(\boldsymbol{q}) = u_0 + \frac{1}{2}\sum_{\alpha=1}^{3}\left\{K_{\alpha^2} + \frac{1}{12}K_{\alpha^4}q_\alpha^2 + \frac{1}{2}\sum_{\beta=1}^{3}\left[K_{\alpha^2\beta^2}\langle q_\beta^2\rangle + \frac{1}{2}(1-\delta_{\alpha\beta})K_{\alpha^2\beta^2}q_\beta^2\right]\right\}q_\alpha^2, \tag{6}$$

where

$$\langle q_\alpha^2\rangle = \frac{\int \mathrm{d}\boldsymbol{q}\, q_\alpha^2 \exp\{-u(\boldsymbol{q})/\theta\}}{\int \mathrm{d}\boldsymbol{q}\exp\{-u(\boldsymbol{q})/\theta\}}, \tag{7}$$

$$u_0(\boldsymbol{q}) = \frac{K_0}{2} - \frac{1}{8}\sum_{\alpha,\beta=1}^{3} K_{\alpha^2\beta^2}\langle q_\beta^2\rangle\langle q_\alpha^2\rangle, \tag{8}$$

and $\alpha, \beta$ denote the coordinates $x, y, z$.

For a crystal having a cubic lattice, $\langle q_\alpha^2\rangle = \langle q^2\rangle/3$. So, the self-consistent potential (1) can be written, in spherical coordinates, as

$$u(q) = u_s(q) + u_{as}(q, \upsilon, \varphi), \tag{9}$$

where the first term denotes the spherically symmetrical part while the second term denotes the angular dependent part of the self-consistent potential $u(q)$. The contributions of the angular dependent part to the thermodynamic properties of crystals are expected to be very small, and they will not be considered here. So, the self-consistent potential will be approximated by the spherically symmetric part only. On the other hand, $u_s(q)$ has the form

$$u_s(q) = \sum_{l=0}^{5}\frac{1}{l!}u_l q^l, \tag{10}$$

where for $l = 2m+1$, $m$ being 0, 1 and 2, $u_l = 0$,

$$u_2 = K_2 + K_4\frac{5\langle q^2\rangle}{18}; \quad u_4 = K_4, \tag{11}$$

and for $l=0$:

$$u_0 = \frac{K_0}{2} - \frac{5}{72}K_4\langle q^2\rangle\langle q^2\rangle \tag{12}$$

with $K_{2i} = \dfrac{\Delta^{2i}K(\boldsymbol{q})}{2i+1}$ at $\boldsymbol{q}=0$ where $\Delta$ is the Laplacian for the coordinate.

The summation in the self-consistent potential $u$ can be restricted to 4, as in the case of an isotropic interaction odd terms of $K$ are zero. In that case $\langle q^m\rangle$ and $u_m$ are also zero for odd $m$'s.

One finds the self-consistent potential

$$u(q) = K_0/2 + K_2 q^2/2 + K_4(q^4/24 + 5q^2\langle q^2\rangle/36 - 5\langle q^2\rangle^2/72). \tag{13}$$

Note that we can use this potential as a "crystal field", which is temperature-dependant through $\langle q^2\rangle$, having an effective depth

$$K_{0\mathrm{eff}} = K_0/2 - 5K_4\langle q^2\rangle^2/72 \tag{14}$$

and an effective curvature

$$K_{2\mathrm{eff}} = K_{2+}5K_4\langle q^2\rangle/18. \tag{15}$$

## III. The 2D Quartic Self-Consistent Potential

In the case of a two-dimensional system we have

$$u(\boldsymbol{q}) = u_0 + \sum_{l+m=1}^{5} F_{x^l y^m}\frac{q_x^l q_y^m}{l!\,m!} \tag{1 bis}$$

with

$$F_{x^l y^m} = \sum_{i+j=0}^{5-l-m} K_{x^{i+l}y^{j+m}}\frac{(-1)^{i+j+k}\langle q_x^i q_y^j\rangle}{i!\,j!}, \tag{2 bis}$$

$$\langle q_x^i q_y^j\rangle = \int q_x^i q_y^j w(\boldsymbol{q})\,\mathrm{d}\boldsymbol{q} \tag{3 bis}$$

$$K_{x^i y^j} = \frac{\partial^{i+j}K(q)}{\partial q_x^i\,\partial q_y^j}, \tag{4 bis}$$

$$K(\boldsymbol{q}-\boldsymbol{q}') = \sum_{\boldsymbol{n}\neq 0}\Phi(\boldsymbol{q}-\boldsymbol{q}'-A\boldsymbol{n}). \tag{5 bis}$$

For crystals possessing two symmetry planes $X=0$ and $Y=0$, (1 bis) can be written as

$$u(\boldsymbol{q}) = u_0 + \frac{1}{2}\sum_{\alpha=1}^{2}\left\{K_{\alpha^2} + \frac{1}{12}K_{\alpha^4}q_\alpha^2 + \frac{1}{2}\sum_{\beta=1}^{2}\left[K_{\alpha^2\beta^2}\langle q_\beta^2\rangle + (1-\delta_{\alpha\beta})K_{\alpha^2\beta^2}q_\beta^2\right]\right\}q_\alpha^2, \tag{6 bis}$$

where

$$\langle q_\alpha^2\rangle = \frac{\int \mathrm{d}\boldsymbol{q}\, q_\alpha^2\exp\{-u(\boldsymbol{q})/\theta\}}{\int \mathrm{d}\boldsymbol{q}\exp\{-u(\boldsymbol{q})/\theta\}}, \tag{7 bis}$$

$$u_0(\boldsymbol{q}) = \frac{K_0}{2} - \frac{1}{8}\sum_{\alpha,\beta=1}^{2}K_{\alpha^2\beta^2}\langle q_\beta^2\rangle\langle q_\alpha^2\rangle, \tag{8 bis}$$

and $\alpha, \beta$ denote the coordinates $x, y$.

For a crystal having a hexagonal lattice, the self-consistent potential (1 bis) can be written, in polar coordinates, as

$$u(q) = u_s(q) + u_{as}(q, \varphi), \tag{9 bis}$$

where the first term denotes the circular symmetrical part while the second term denotes the angular dependent part of the self-consistent potential $u(q)$. The contributions of the angular dependent part to the thermodynamic properties of crystals are expected to be very small, and they will not be considered here. So, the self-consistent potential will be approximated by the circularly symmetrical part only. On the other hand, $u_s(q)$ has the form

$$u_s(q) = \sum_{l=0}^{5} \frac{1}{l!} u_l q^l, \tag{10 bis}$$

where for $l = 2, 4$

$$u_2 = K_2 + K_4 \frac{\langle q^2 \rangle}{3}; \quad u_4 = K_4, \tag{11 bis}$$

and for $l = 0$

$$u_0 = \frac{K_0}{2} - \frac{1}{12} K_4 \langle q^2 \rangle^2 \tag{12 bis}$$

with

$$K_2 = \frac{1}{2} \sum_{\alpha=1}^{2} K_{\alpha^2},$$

$$K_4 = \frac{3}{8} \sum_{\alpha,\beta=1}^{2} K_{\alpha^2 \beta^2}$$

*at* $\boldsymbol{q} = 0$ and $\langle q_x^2 \rangle = \langle q_y^2 \rangle = \langle q^2 \rangle / 2$.

One finds the self-consistent potential

$$u(q) = K_0/2 + K_2 q^2/2 + K_4 (q^4/24 + q^2 \langle q^2 \rangle / 6 - \langle q^2 \rangle^2 / 12). \tag{13 bis}$$

Note that we can use this potential as a "crystal field", which is temperature-dependant through $\langle q^2 \rangle$, having an effective depth

$$K_{0\text{eff}} = K_0/2 - K_4 \langle q^2 \rangle^2 / 12 \tag{14 bis}$$

and an effective curvature

$$K_{2\text{eff}} = K_2 + K_4 \langle q^2 \rangle / 3. \tag{15 bis}$$

## IV. The Self-Consistency of Amplitude

We ask now for the self-consistency of $\langle q^2 \rangle$, the amplitude of atomic vibrations:

$$\langle q^2 \rangle = \frac{\int \mathrm{d}q\, q^{d+1} \exp\{-u(q)/\theta\}}{\int \mathrm{d}q\, q^{d-1} \exp\{-u(q)/\theta\}} \tag{16}$$

with $d$ being the dimension of the studied system.

The calculation of $\langle q^2 \rangle$ (see part I of this work) can be done in two ways: a) Exactly by introducing a single auxiliary function and b) approximatively by successive approximation starting directly from the quasi-harmonic approximation and by the application of $\varepsilon$-algorithm [5–7].

In order to give the exact value of $\langle q^2 \rangle$, let us write

$$t = q^2 \sqrt{\frac{K_4}{12\theta}}, \quad y = u_2 \sqrt{\frac{3}{K_4 \theta}}. \tag{17}$$

Then we can express the integrals

$$\int \mathrm{d}q\, q^i \exp\{-u(q)/\theta\}$$

in terms of parabolic cylinder functions **D** (see the appendix in part I):

$$\int \mathrm{d}q\, q^i \exp\{-u(q)/\theta\} = \exp\{-(u_0 + y^2/4)/\theta\} \cdot \left\{ 12\theta/(K4)^{i/4 - 1/4}\, \Gamma\left(\frac{i+1}{2}\right) \mathbf{D}_{-(l+1)/2}(y) \right\}.$$

So (16) could be written as

$$\sqrt{\frac{K_4}{3\theta}} \langle q^2 \rangle = \mathrm{d} \frac{\mathbf{D}_{-(d/2+1)}(y)}{\mathbf{D}_{-d/2}(y)}. \tag{18}$$

Let us now introduce

$$S_d(y) = \mathrm{d} \frac{\mathbf{D}_{-(d/2+1)}(y)}{\mathbf{D}_{-d/2}(y)} \tag{19}$$

with

$$y = X + \frac{(d+2) S_d(X)}{2d}, \tag{20}$$

where $S_d$, *is a universal function of the normalized quartic strength* $1/X$ by the implicit equation

$$S_d(X) = \mathrm{d} \frac{\mathbf{D}_{-(d/2+1)}\left[ X + \frac{(d+2) S_d(X)}{2d} \right]}{\mathbf{D}_{-d/2}\left[ X + \frac{(d+2) S_d(X)}{2d} \right]}. \tag{21}$$

On the other hand, if we restrict ourself to the case of the potential of interactions with a positive second derivative (Lennard-Jones central pairwise potential) and assume that the relation $K_4 \theta < 3 (K_2)^2$ holds, the amplitude of atomic vibrations $\langle q^2 \rangle$ could be expressed in a series of the form (this procedure is discussed in details in part I)

a) For $d = 3$:

$$\langle q^2 \rangle = 3 \sqrt{\frac{3\theta}{K_4}} \left( 1 - \frac{5}{X^2} + \frac{52.5}{X^4} - \frac{713.75}{X^6} \right.$$

$$+\frac{11196.875}{X^8}-\frac{193495.3125}{X^{10}} \tag{22}$$
$$+\frac{3600978.9063}{X^{12}}+\frac{71311510.5469}{X^{14}}+\ldots\Big).$$

b) For $d=2$:

$$\langle q^2\rangle = 2\sqrt{\frac{3\theta}{K_4}}\Big(1-\frac{4}{X^2}+\frac{34}{X^4}-\frac{378}{X^6}+\frac{4998}{X^8} \tag{23}$$
$$-\frac{70666}{X^{10}}+\frac{1111050}{X^{12}}+\frac{18839442}{X^{14}}+\ldots\Big).$$

The series (23) and (24) are diverging, but one can circumvent this difficulty through the use of the $\varepsilon$-algorithm [5–7]. Then, if we introduce the function $S_{d,\varepsilon}$ defined by

$$S_{d,\varepsilon}=\langle q^2\rangle/\sqrt{3\theta/K_4}\,, \tag{24}$$

we can express the amplitude of atomic vibrations, other moments of the distribution function, the equations of state and thermodynamic properties by the same formulae, but for the approximative approach $S_d$ should be replaced by $S_{d,\varepsilon}$. Here, it is important to mention that $S_d$ and $S_{d,\varepsilon}$ obey the same differential equation of first order:

$$\frac{\mathrm{d}\Sigma_d}{\mathrm{d}X}=\frac{2\left[-d+X\Sigma_d+\dfrac{(d+1)}{d}\Sigma_d^2\right]}{d+4-\dfrac{(d+2)}{d}\Sigma_d\left[X+\dfrac{(d+1)}{d}\Sigma_d\right]}, \tag{25}$$

where $\Sigma_d=S_d$ or $S_{d,\varepsilon}$ depends on the used approximation.

Other moments of the distribution function can be obtained using the recursion

$$\langle q^{2p}\rangle = 2(3\theta/K_4)^{1/2}\left[(2p-1)(3\theta/K_4)^{1/2}\langle q^{2(p-2)}\rangle\right.$$
$$\left.-y\langle q^{2(p-1)}\rangle\right] \tag{26}$$

with taking into account that $\langle q^0\rangle=1$.

## V. Thermodynamic Properties of the Studied Systems

In the approximation considered with taking into account the quantum corrections only, the equations of state of an infinite perfect crystal can be written in the form

$$P_d = P_{0d}+P_{Qd}, \tag{27}$$
$$E_d = E_{0d}+E_{Qd}, \tag{28}$$

where

$$P_{0d} = -\frac{a}{2dV_d}\left\{\frac{\mathrm{d}K_0}{\mathrm{d}a}+X\Sigma_d(X)\theta\frac{\mathrm{d}\,\mathrm{Ln}\,K_2}{\mathrm{d}a}\right.$$
$$\left.+\frac{\theta[d-X\Sigma_d(X)]}{2}\frac{\mathrm{d}\,\mathrm{Ln}\,K_4}{\mathrm{d}a}\right\}, \tag{29}$$

$$P_{Qd} = -\frac{h^2a}{24d\pi^2\theta mV_d}\frac{\partial}{\partial a}\langle\Delta_q u(q)\rangle, \tag{30}$$

$$E_{0d}=\frac{N}{2}\left\{K_0+\frac{\theta[3d+X\Sigma_d(X)]}{2}\right\}, \tag{31}$$

$$E_{Qd}=\frac{Nh^2}{24\pi^2\theta m}\frac{\partial}{\partial T}\langle\Delta_q u(q)\rangle \tag{32}$$

with $V_d$ being the $d$-dimensional volume of the unit cell. The terms $\frac{\partial}{\partial a}\langle\Delta_q u(q)\rangle$ and $\frac{\partial}{\partial T}\langle\Delta_q u(q)\rangle$ can be calculated easily by using (13), (13 bis), (25) and the derivatives of $X$:

$$\frac{\partial X}{\partial a}=X\left(\frac{1}{K_2}\frac{\mathrm{d}K_2}{\mathrm{d}a}-\frac{1}{2K_4}\frac{\mathrm{d}K_4}{\mathrm{d}a}\right);\quad \frac{\partial X}{\partial\theta}--\frac{X}{2\theta}. \tag{33}$$

Thus, the isochoric specific heat and the isothermal bulk modulus take the form

$$C_{vd}=C_{v0d}+C_{vQd}, \tag{34}$$
$$B_{Td}=B_{T0d}+B_{TQd}, \tag{35}$$

where

$$B_{Tid}=-V_d\frac{\partial P_{id}}{\partial V_d}, \tag{36}$$

$$C_{vid}=\frac{\partial E_{id}}{\partial T} \tag{37}$$

with $i$ being equal 0, $Q$, or nothing.

The volume thermal expansion coefficient, the isobaric specific heat and the adiabatic bulk modulus, with the quantum corrections, can be calculated using the familiar thermodynamic relations:

$$\beta_d = \frac{1}{V_d}\frac{\partial V_d}{\partial T}=\frac{1}{B_{Td}}\frac{\partial P_d}{\partial T}, \tag{38}$$

$$C_{pd}=C_{vd}+TB_{Td}V_d\beta_d^2, \tag{39}$$

$$B_{sd}=\frac{B_{Td}C_{pd}}{C_{vd}}. \tag{40}$$

## VI. Numerical Results and Discussion

The calculation of $S_d(X)$ and $S_{d,\varepsilon}(X)$, with $d=2$ and 3 is demonstrated in Fig. 1, where we see that

there is a remarkable agreement between these functions when $X > 0$ (i.e. $K_2 > 0$), while it is questionable when $X < -1$ (i.e. $K_2 < 0$). So, the proposed method could be applied with a very good precision when we deal with a potential of interactions which has a positive second derivative (this is the case of the Lennard-Jones central pairwise potential).

We have computed the equilibrium nearest-neighbour distances in inert gas solids versus temperature at zero pressure. In our calculations, the Lennard-Jones effective 6–12 potential is used, with the separation at the minimum and the depth of the potential well being taken from [8, 9].

Solving numerically the equation

$$P_d = 0, \tag{41}$$

the equilibrium nearest-neighbour distance $a(T)$ is computed. Equation (41) has two roots $a_1(T) \leqq a_2(T)$. These two roots coincide at the temperature $T_{sd}(P_d)$. The lower branch $a = a_1(T)$ of the isobar represents the stable thermodynamic states $(\partial a_1/\partial P)_T < 0$, while the upper branch represents the unstable ones. At the spinodal point $a = a(T_s)$ of the isobar $(\partial a/\partial P)_T \to \infty$. All potentials in use give values $T_{s3}(P) > T_{m3}(P)$. For example, if we use the following parameters:

for Ne: $\varepsilon/k_B = 35.6$ K; $\sigma = 2.78$ Å,
for Ar: $\varepsilon/k_B = 142.0$ K; $\sigma = 3.4389$ Å,
for Kr: $\varepsilon/k_B = 202.0$ K; $\sigma = 3.635$ Å,
for Xe: $\varepsilon/k_B = 281.0$ K; $\sigma = 3.964$ Å

of L-J potential we obtain

| | Ne | Ar | Kr | Xe |
|---|---|---|---|---|
| $T_m$ (K) | 24.33 | 83.806 | 115.763 | 161.391 |
| $T_{s3}$ (K) | 31.92 | 127.34 | 181.15 | 252.0 |
| $T_{s2}$ (K) | 21.79 | 86.94 | 123.68 | 172.06 |
| $T_{s3}/T_{m3}$ | 1.3120 | 1.5195 | 1.5648 | 1.5614 |
| $T_{s2}/T_{s3}$ | 0.6826 | 0.6827 | 0.6827 | 0.6828 |

So, if we exclude Ne, where quantum effects are considerable up to the melting point, we find that $T_s$ is about 1.55 times $T_m$ for Ar, Kr, and Xe. On the other hand it is shown that $T_{s2}/T_{s3}$ is constant for all studied crystals. This constant can be expected to be the upper value of the ratio $T_{m2}/T_{m3}$. Moreover, the influence of vacancy formation with temperature in the case of two-dimensional systems is much bigger than that in the case of 3d bulk solid. Thus, the melting temperature of 2d inert gases solids (Ar, Kr, and Xe) can be evaluated to be considered in the interval

$$C_1\, T_{m3}\, T_{s2}/T_{s3} < T_{m2} < T_{m3}\, T_{s2}/T_{s3}, \tag{42}$$

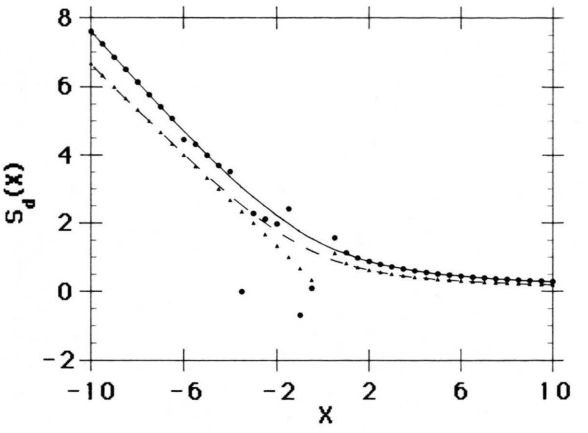


Fig. 1. The $S_3$ (−), $S_{3,\varepsilon}$ (●), $S_2$ (− −), $S_{2,\varepsilon}$ (▲) functions.

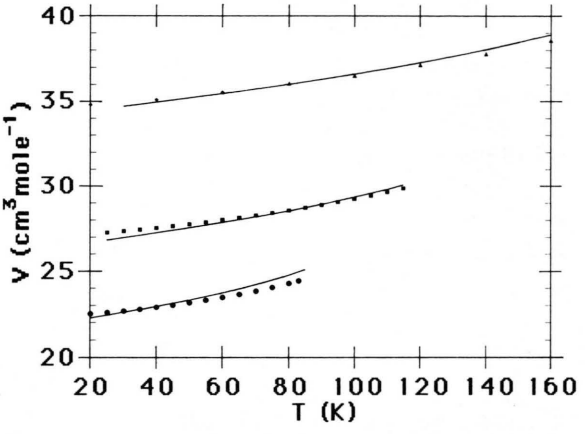


Fig. 2. The molar volume of three-dimensional Ar, Kr and Xe. Full lines denote the calculated values while experimental data are denoted by (●) [12] for Ar, by (■) [13] for Kr and by (♦) [14], and (▲) [15] for Xe.

where $C_1$ is a constant of order unity. If we give the lower predicted value $C_1 = 0.9$, formula (42) leads to the following results for $T_{m2}$: Ne ($14.95 < T_{m2} < 16.61$); Ar ($51.489 < T_{m2} < 57.21$); Kr ($71.525 < T_{m2} < 79.472$); Xe ($98.934 < T_{m2} < 109.927$). These results are in a good agreement with the experimental ones (see for example [10]) and somehow affirm the predictions of Persson [11].

Along the lower branch of the isobar we have calculated the thermoelastic properties of argon, krypton and xenon up to the melting points of three-dimensional crystals or up the upper predicted values of melting points of two-dimensional crystals. The cor-

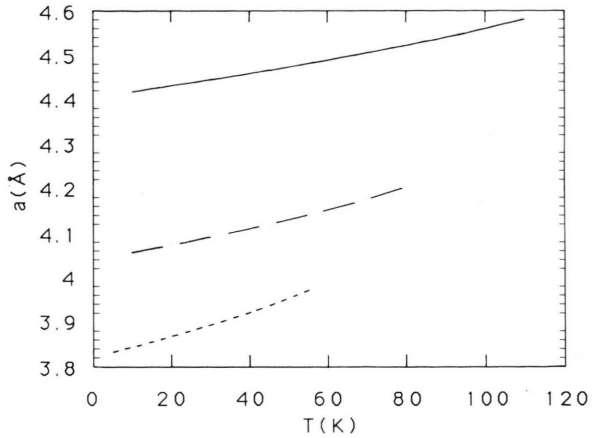


Fig. 3. The nearest neighbour distances in two-dimensional crystals: (- - -) for Ar; (— —) for Kr; (—) for Xe.

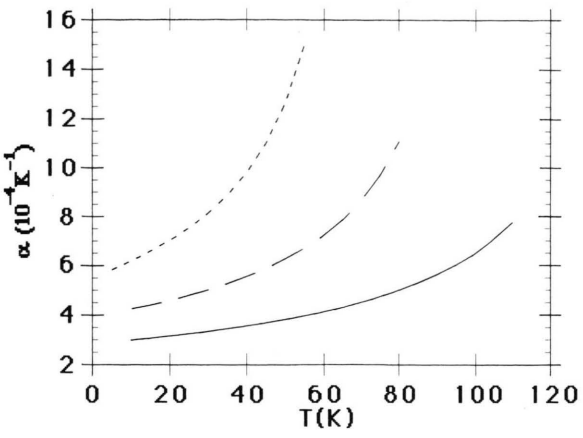


Fig. 5. The linear thermal expansion of two-dimensional crystals (- - -) for Ar; (— —) for Kr; (—) for Xe.

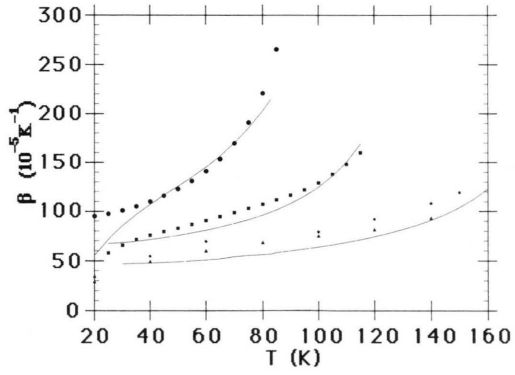


Fig. 4. The volume thermal expansion of three-dimensional Ar, Kr, and Xe. Full lines denote the calculated values while experimental data are denoted by (●) [12], for Ar, by (■) [13] for Kr and by (♦) [14], and (▲) [15] for Xe.

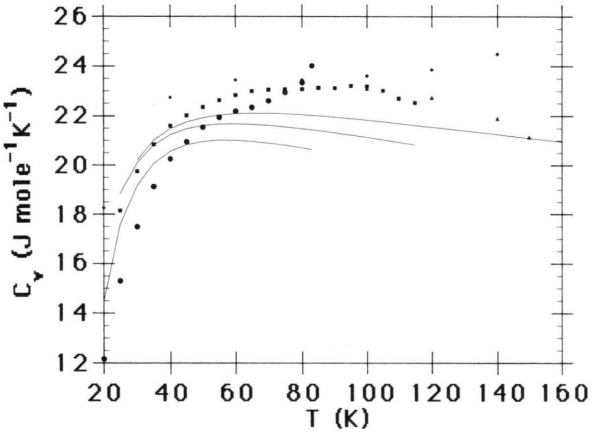


Fig. 6. The isochoric specific heat of three-dimensional Ar, Kr and Xe. Full lines denote the calculated values while experimental data are denoted by (●) [12] for Ar, by (■) [13] for Kr and by (♦) [15], and (▲) [16] for Xe.

rections due to quantum effects are considered in our calculations. We show the calculations of the molar volumes (Fig. 2), the nearest neighbour distances of two-dimensional crystals (Fig. 3), the volume thermal expansions (Fig. 4), the linear thermal expansion in two-dimensional crystals (Fig. 5) and the isochoric specific heats of three-dimensional (Fig. 6) and two-dimensional inert gases. Available experimental data are also given on these figures. The experimental data are taken from [12–16] for three-dimensional crystals. Unfortunately, we miss experimental data related to two-dimensional inert gases, to compare our results with them.

It is clear from Figs. 2, 4, and 6 that the calculated properties of crystalline Ar, Kr and Xe are in a good agreement with their experimental values. Concerning other thermodynamic properties we found that: 1) For the potential energy there is an excellent accord with experiment at low and moderate temperatures, and the calculated results differ from the experimental values at the melting points by less than 1.7%. 2) The agreement of bulk modulus $B_T$ and $B_s$ with the experimental data is within the experimental errors, which are about 10% at high temperatures [12]. Our calculated results (first values) and the experimental results (second values) of the adiabatic bulk modulus

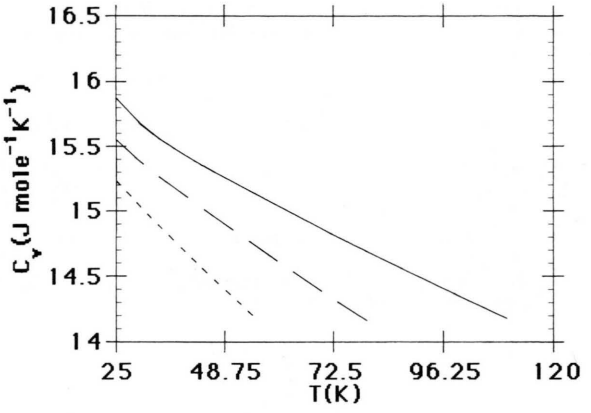


Fig. 7. The isochoric specific heat of two-dimensional crystals: (- - -) for Ar; (— —) for Kr; (—) for Xe.

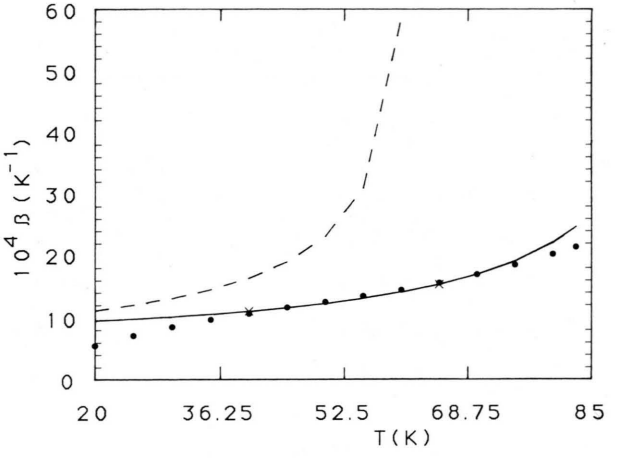


Fig. 8. The volume thermal expansion of Ar: (●) [12] experimental data, (—) calculated results using $S_3$, (— — ×) calculated results using $S_{3,\varepsilon}$ and (- - -) calculated results using quasi-harmonic approximation.

for Ar at 82 K, Kr at 100 K and Xe at 156 K are $B_s = 17.73 \times 10^8$ N/m$^2$, $B_s = 17.699 \times 10^8$ N/m$^2$ [12]; $B_s = 21.882 \times 10^8$ N/m$^2$, $B_s = 22.272 \times 10^8$ N/m$^2$ [17]; $B_s = 22.272 \times 10^8$ N/m$^2$, $B_s = 22.624 \times 10^8$ N/m$^2$ [18].

## VI. Conclusion

In summary the use of the $S_{d,\varepsilon}$ function enables one to calculate the properties of the rare-gas solids with quartic interactions. The amplitude of atomic vibrations $\langle q^2 \rangle$, calculated on the basis of the quasi-harmonic approximation, has a diverging expansion for high temperatures or small $X$. One is then not surprized to find that it is not worthwhile to go beyond the quasi-harmonic approximation, except for small ranges of temperatures where the gain is indeed not significant. It is demonstrated here that one can circumvent this difficulty through the use of the $\varepsilon$-algorithm: the range of validity grows then to have, really, the same order of other anharmonic theories [19–21]. The calculations, made using the approximative approach, do not differ from those made using the precise approach by more than 0.2% at the melting points. This result is demonstrated for the thermal volume expansion of argon on Fig. 8, where we give also the calculations made using the quasi-harmonic approximation. It is seen from this figure that the quasi-harmonic approximation is not applicable at temperatures higher than $T_m/2$, which is a quite known result.

The discrepancies between our calculations and experiment are very small (within the experimental errors). It is expected that the agreement between the theoretical and experimental values of some properties can be ameliorated to be nearly perfect by taking into consideration the angular dependent part of the self-consistent potential and the formation of vacancies with increasing temperature.

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