Anharmonic Self-Consistent Theory of Crystals.
I. A 1d Quartic Crystal Model

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We apply the Unsymmetrized Self-Consistent-Field-Method (USCFM) to a linear infinite chain of identical atoms with a quartic pair interaction potential. We show that an exact solution of the USCFM can be found in terms of a single auxiliary function $\mathcal{S}_1$ which is studied here in details. We use it to calculate the partition function, the energy and the free energy, the moments of the position, the corrections due to quantum effects and higher terms of the potential, the specific heat and the thermal expansion. An anharmonic approximative approach, based on the self-consistent potential of the used method, is developed also. We apply these two approaches to the study of the thermo-elastic properties of a one dimensional system (krypton). It is demonstrated that the approximate approach is very effective when dealing with pairwise potentials of positive second derivative. The Lennard-Jones potential is used in our calculations.

Key words: Linear chain; Anharmonicity; Thermodynamic properties; Inert gases.

I. Introduction

The Self-Consistent Field-Method (SCFM) replaces interaction potentials by single-particle potentials, and the main hypothesis is always the representation of the wave function by a product of one-particle wave functions. This product could be symmetrized, but generally this would lead to considerable difficulties, and the wave functions of the SCFM are mostly left Unsymmetrized (USCFM). On the one hand this last restriction is clearly very contestable for problems with coherence over large distances, such as perfect solids; it is possible to go beyond and take into account symmetrization as a perturbation [1] (cf. also section IV), but the expansions for an infinite perfect solid, for example, are far from being convergent. On the other hand, as soon as some localization is working, the USCFM is quite adequate: impurities in solids, surfaces of solids, adsorption, solid mixtures and some aspects of liquids are relevant applications for it. One of the still pending problems for its use as an easy and quick tool is not only to dispose of approximate ways of calculation, but also to verify their pertinence, at least inside the USCFM. For example, to study a perfect if anharmonic solid, one often looks for an expansion with respect to the anharmonicity, e.g. a quartic term in the potential relative to the harmonic part [2]. For strong anharmonicity this expansion has no reason to work correctly, but moreover we became aware that it does not even converge. On the whole, exact solutions for some kinds of potentials at least are badly needed. We therefore devote this paper to the exact solution for a pair interaction with harmonic and quartic terms, acting in an *infinite chain of identical atoms* (indeed the infinite limit for N atoms along a large circle); a forthcoming paper is devoted to 2d and 3d solids with some symmetry and similar (isotropic) interactions.

This solution was used in a study of adsorption with the USCFM as a model of strongly anharmonic perfect crystals (the semi-infinite crystals with or without adsorbed species will be presented elsewhere). They also could be useful as a starting point to tackle more exactly many problems (impurities, phonon collision, localized modes, …) and at least to appreciate the validity of other approximations.

We first recall the basic equations of the USCFM (§ II) and the corresponding thermodynamics (§ III),

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how to improve it by calculating the corrections due to quantum effects and higher terms of the potential (§ IV). Then we show how to produce an exact solution in the USCFM approximation for an interaction potential including fourth order terms (or even fifth order ones, as the odd terms do not contribute to the energy of a perfect crystal), i.e. the quartic model (§ V).

We emphasize that this solution can be expressed in terms of *a single universal transcendental function* $\mathscr{S}_1$ which can be implicitly expressed in terms of parabolic cylinder functions, but we show that it can be rather calculated directly by integrating a first order differential equation; we give different properties and approximations of $\mathscr{S}_1$ in the appendix.

We use it effectively to calculate equations of state and thermoelastic properties of an infinite chain of identical atoms with and without the correlation and quantum corrections (§ V). The case of weak anharmonicity is detailed (§ VI) for comparison with previous results. Expansions for strong anharmonicity are discussed (§ VII). It will be shown that traditional expansions are quite limited; we shall mention that, using a procedure of acceleration of convergence [3–5], especially the ε-algorithm, allows one to obtain excellent approximations for this diverging series. As there is no theoretical foundation to the extension of these procedures to divergent series, it is worthwhile to have the exact result to appreciate the validity of this fancy mathematics.

II. Basic Equations

The first assumption in the USCFM [2, 6, 7] is the *factorizibility* of the wave function (i.e. it can be unsymmetrized, as long as the overlaps of individual wave functions are so small that symmetrization has no influence). Moreover, if we work in the classical limit, this factorizibility is valid for the probability of presence or the density function. Let us call $\boldsymbol{r}, \boldsymbol{p}$ the set of coordinates $\{\boldsymbol{r}_i, \boldsymbol{p}_i\}$, $\boldsymbol{r}_i$ and $\boldsymbol{p}_i$ being the coordinates and momenta of the i-th atom; the factorizibility of the density function $\boldsymbol{W}(\boldsymbol{r}, \boldsymbol{p})$ can be written

$$\boldsymbol{W}(\boldsymbol{r}, \boldsymbol{p}) = \prod_i \{W_i(\boldsymbol{r}_i, \boldsymbol{p}_i)\} \tag{1}$$

where $W_i(\boldsymbol{r}_i, \boldsymbol{p}_i)$ is the probability of the presence of the i-th atom.

In many cases, to which we shall restrict ourselves here (classical limit, absence of magnetic fields, ...), the kinetic and potential parts can be separated; we write, for a particle of mass m_i

$$W_i(\boldsymbol{p}_i, \boldsymbol{r}_i) = (2\pi m_i \theta)^{-d/2}\, e^{-\boldsymbol{p}_i^2/(2m_i\theta)}\, w_i(\boldsymbol{r}_i)\,, \tag{2}$$

$$\int W_i(\boldsymbol{p}_i, \boldsymbol{r}_i)\, \mathrm{d}\boldsymbol{p}_i = w_i(\boldsymbol{r}_i) \tag{2 bis}$$

with $\theta = k_{\mathrm{B}}T$. d denotes the dimension of the system. Moreover, the kinetical part can be integrated out to θ in the classical limit, not only in the probability function, as it has been done in (2 bis), but also in the partition function or in any thermodynamic function, as will be done later.

For a perfect crystal, all one-particle probability densities have the same form, but they are shifted in arguments by the lattice displacement vectors

$$w_i(\boldsymbol{r}_i) = w(\boldsymbol{q}_i); \quad \boldsymbol{q}_i = \boldsymbol{r}_i - \boldsymbol{R}_i \tag{3}$$

with $\boldsymbol{R}_i = \hat{A}\,\boldsymbol{n}_i$. $\hat{A}$ is the lattice matrix and $\boldsymbol{n}_i$ are vectors having integer components. This means that we work on a fundamental state with maximum symmetry (i.e. corresponding to the identity representation of the translation group) or stationary case. In the case of the infinite chain, all $w_i(r_i)$ can be written $w(q_i)$ with

$$w_i(r_i) \ldots w(q_i), \quad q_i = r_i - R_i\,, \tag{3 bis}$$

where $R_i = (\boldsymbol{a}\, i)$ are the central position, on the 1 d one and only Bravais lattice, with lattice parameter a.

For a pairwise interaction between the i-th and j-th atoms $f^{ij}(|\boldsymbol{r}_i - \boldsymbol{r}_j|) \equiv f(|\boldsymbol{r}_i - \boldsymbol{r}_j|)$, the Self-Consistent individual mean-Fields in this method are to be derived from the self-consistent potentials $u_i(\boldsymbol{r}_i)$ given by averaging the energy of interaction with the other atoms j according to their density of presence $w_j(\boldsymbol{r}_j)$:

$$u_i(\boldsymbol{r}_i) = \sum_{j \neq i} \int f^{ij}(|\boldsymbol{r}_i - \boldsymbol{r}_j|)\, w_j(\boldsymbol{r}_j)\, \mathrm{d}\boldsymbol{r}_j - \langle u_i \rangle\,, \tag{4}$$

where $\langle\ \rangle$ means the average over $\boldsymbol{q}$ and the second term is a constant, which adapts the zero of potential, essentially preventing to count two times the pair interaction. One can be easily find that

$$\langle u_i \rangle \equiv \langle u \rangle = 1/2 \sum_{j \neq i} \iint f(|\boldsymbol{r}_i - \boldsymbol{r}_j|)\, w_i(\boldsymbol{r}_i)\, w_j(\boldsymbol{r}_j)\, \mathrm{d}\boldsymbol{r}_i\, \mathrm{d}\boldsymbol{r}_j\,. \tag{4 bis}$$

Taking into account the translational symmetry, all $u_i(\boldsymbol{r}_i)$ can be written $u(\boldsymbol{q}_i)$, a single *self-consistent potential* given by

$$u(\boldsymbol{q}_i) \equiv u(\boldsymbol{q}) = \sum_{\boldsymbol{n} \neq 0} \iint f(|\boldsymbol{q} - \boldsymbol{q}' - \hat{A}\boldsymbol{n}|)\, w(\boldsymbol{q}')\, \mathrm{d}\boldsymbol{q}' - \langle u \rangle \tag{5}$$

with

$$\langle u \rangle = 1/2 \sum_{\boldsymbol{n} \neq 0} \iint f(|\boldsymbol{q} - \boldsymbol{q}' - \hat{A}\boldsymbol{n}|)\, w(\boldsymbol{q})\, w(\boldsymbol{q}')\, \mathrm{d}\boldsymbol{q}\, \mathrm{d}\boldsymbol{q}'\,. \tag{5 bis}$$

The summation over the different neighbours can be done before any other calculation by introducing

$$K(\boldsymbol{x}) = \sum_{n \neq 0} f(|\boldsymbol{x} - \hat{A}\boldsymbol{n}|)\,, \tag{6}$$

resulting in

$$u(\boldsymbol{q}) = \int K(\boldsymbol{q} - \boldsymbol{q}')\, w(\boldsymbol{q}')\, \mathrm{d}\boldsymbol{q}' - \langle u \rangle \tag{7}$$

with

$$\langle u \rangle = 1/2 \iint K(\boldsymbol{q} - \boldsymbol{q}')\, w(\boldsymbol{q})\, w(\boldsymbol{q}')\, \mathrm{d}\boldsymbol{q}\, \mathrm{d}\boldsymbol{q}'\,. \tag{7bis}$$

On the other hand, the following estimation of the probability of presence at temperature T is used [6]:

$$w(\boldsymbol{q}) = \frac{\exp\{-u(\boldsymbol{q})/\theta\}}{z(\theta, \boldsymbol{a})} \tag{8}$$

with the normalization constant $z(\theta, \boldsymbol{a})$, which is really the partial partition function for the potential energy of one single atom:

$$z(\theta, \boldsymbol{a}) = \int \exp\{-u(\boldsymbol{q})/\theta\}\, \mathrm{d}\boldsymbol{q}\,. \tag{9}$$

Note that the way in which $\boldsymbol{W}(\boldsymbol{r}, \boldsymbol{p})$ separates is self-consistent. It depends on all variables; $W_i(\boldsymbol{r}_i, \boldsymbol{p}_i)$ or $w(\boldsymbol{q})$ can be thought, like $z(\theta, \boldsymbol{a})$, as depending on the mean positions $\boldsymbol{R}_i$ of other atoms (or only the lattice parameter $\boldsymbol{a}$ for the perfect crystal), and also on their deviation from them, naturally, i.e. of the temperature.

The *self-consistency* can be written for the probability of presence $w(\boldsymbol{q})$, substituting (7) into (8):

$$z(\theta, \boldsymbol{a})\, w(\boldsymbol{q}) \tag{10}$$
$$= \exp\{-1/\theta \int K(\boldsymbol{q} - \boldsymbol{q}')\, w(\boldsymbol{q}')\, \mathrm{d}\boldsymbol{q}'\} \exp\{\langle u \rangle/\theta\}\,,$$

$$\int w(\boldsymbol{q})\, \mathrm{d}\boldsymbol{q} = 1\,. \tag{11}$$

But it could also be written for the self-consistent field $u(\boldsymbol{q})$, inversely substituting (8) into (7). Later on we shall find it easier to write the self-consistency for $\langle q^2 \rangle$. We have just to remember that for our problem a single self-consistency equation is needed.

III. Thermodynamics of the USCFM

The USCFM approximation does not take account of any correlation or quantum effect. The thermodynamic functions are based on the individual self-consistent potentials. One can use a "zero order" partition function $\boldsymbol{Z}_0(\theta, \boldsymbol{a})$:

$$\boldsymbol{Z}_0(\theta, \boldsymbol{a}) = \prod_i Z_i(\theta, \boldsymbol{a})\,, \tag{12}$$

where all the partial partition functions $Z_i(\theta, \boldsymbol{a})$ are equal:

$$Z_i(\theta, \boldsymbol{a}) \equiv Z(\theta, \boldsymbol{a}) \tag{13}$$
$$= h^{-d} \iint \exp\{-[\boldsymbol{p}^2/2m + u(\boldsymbol{q})]/\theta\}\, \mathrm{d}\boldsymbol{q}\, \mathrm{d}\boldsymbol{p}\,,$$

h being the Planck constant.

The kinetical part can be integrated out:

$$Z(\theta, \boldsymbol{a}) = (2\pi m \theta/h^2)^{d/2}\, z(\theta, \boldsymbol{a})\,. \tag{14}$$

We shall use essentially the "potential one-atom" partial partition function $z(\theta, \boldsymbol{a})$ given by (9).

The Helmholtz free energy F_0, in this zero order approximation, is derived by [6, 7]:

$$F_0 = -\theta \ln[\boldsymbol{Z}_0(\theta, \boldsymbol{a})] = -\theta N \ln[Z(\theta, \boldsymbol{a})]\,. \tag{15}$$

Writing the Helmholtz relation

$$E_0 = -T^2\, \partial(F_0/T)/\partial T = \theta^2 N\, \partial\big(\ln[Z(\theta, \boldsymbol{a})]\big)/\partial\theta\,, \tag{16}$$

we recover the expected expression for the internal energy E_0:

$$E_0 = U_0 + N\, \mathrm{d}\theta/2\,, \tag{17}$$

calling "self-consistent potential energy of the system" the sum of the individual self-consistent potentials:

$$U_0 = \sum_i \langle u_i(q_i) \rangle = N \langle u \rangle\,. \tag{18}$$

If H is the hamiltonian of the system under study, and if v and V are conjugate variables, i.e. if

$$V = -\partial H/\partial v\,, \tag{19}$$

then in the USCFM approximation [1]

$$V_0 = \langle V \rangle = -\langle \partial H/\partial v \rangle = -\partial F_0/\partial v\,. \tag{20}$$

We introduce the "linear pressure" $\mathscr{A}$ as the *average* conjugate of the length $(N\boldsymbol{a})$ of the chain

$$\mathscr{A}_0 = -\partial F_0/\partial(N\boldsymbol{a}) = \theta\, \partial(\ln Z)/\partial\boldsymbol{a}\,. \tag{21}$$

The Gibbs free energy (or free enthalpy) G or the chemical potential μ can then be written

$$G_0 = N\mu_0 = F_0 + N\boldsymbol{a}\,\mathscr{A}_0 = F_0 - \boldsymbol{a}\,\partial F_0/\partial\boldsymbol{a}\,. \tag{22}$$

IV. USCFM Corrections

Formulae (15) to (22) express the thermodynamic properties of the studied system to zero order, i.e. for the present purpose, the noncorrelative approximation. According to Bogoliubov's statistical variational principle [1] they can be extended to give the optimum upper estimation of the Helmholtz free energies if one replaces $\boldsymbol{Z}_0(\theta, \boldsymbol{a})$ by the partition function with inclusion of the actual pair interaction:

$$\boldsymbol{Z}_0(\theta, \boldsymbol{a}) \tag{23}$$

$$= h^{-1} \iint \exp\left\{-\boldsymbol{p}^2/2m\theta - 1/2\theta \sum_i \sum_{i \neq j} f(|\boldsymbol{r}_i - \boldsymbol{r}_j|)\right\} \mathrm{d}\boldsymbol{r}\, \mathrm{d}\boldsymbol{p}$$

$$= (2\pi m\theta/h^2)^{-dN/2} \int \exp\left\{-1/2\theta \sum_i \sum_{i \neq j} f(|\boldsymbol{r}_i - \boldsymbol{r}_j|)\right\} \mathrm{d}\boldsymbol{r}.$$

To get the second order statistical perturbation terms we expand in a power series of $(U - U_0)$; we obtain the correction F_2 [8]:

$$F_2 = F_{\text{corr}} + F_6\,, \tag{24}$$

where

$$F_6 = \langle U - U_0 \rangle \tag{24 bis}$$

is the correction due to terms in the potential energy higher than those which were used to calculate U_0, and

$$F_{\text{corr}} = -1/(2\theta)\langle (U - U_0)^2 \rangle + 1/(2\theta)\langle U - U_0 \rangle^2 + 1/(6\theta^2)\langle U - U_0)^3 \rangle \tag{24 ter}$$

is the correlation correction, where

$$U = 1/2 \sum_i \sum_{i \neq j} f(|\boldsymbol{r}_i - \boldsymbol{r}_j|)\,.$$

It should be mentioned that the last term in F_{corr} is zero for perfect crystals, which is the case here. Naturally, it is also zero if the probability density function is factorizable (zero order approximation).

The correlation correction will not be studied here, as it raises difficult convergence problems which will be discussed elsewhere.

We can also include the quantum correction to the thermodynamic functions. The first quantum correction to the Helmholtz free energy has the form [9]

$$F_Q = \frac{h^2}{96\pi^2\theta} \sum_i \frac{\langle \nabla_i^2 u_i \rangle}{m_i}\,, \tag{25}$$

∇_i^2 being the Laplacian for the coordinate $\boldsymbol{r}_i$ (or $\boldsymbol{q}_i$).

The Helmholtz free energy of the whole system is then

$$F = F_0 + F_{\text{corr}} + F_6 + F_Q\,, \tag{26}$$

and analogous corrections to the other thermodynamic functions are to be taken into account, i.e. we can write (15), (20), (21) or (22), replacing the index 0 by η (η = corr, 6, Q or nothing):

$$E_\eta = \theta^2\, \partial(F_\eta/\theta)/\partial\theta\,, \tag{15 bis}$$

$$\langle V_\eta \rangle = -\partial F_\eta/\partial v\,, \tag{20 bis}$$

$$\mathscr{A}_\eta = -\,\partial F_\eta/\partial(N\boldsymbol{a})\,, \tag{21 bis}$$

$$G_\eta = N\mu_\eta = F_\eta + N\boldsymbol{a}\,\mathscr{A}_\eta = F_\eta - \boldsymbol{a}\,\partial F_\eta/\partial\boldsymbol{a}\,. \tag{22 bis}$$

Up to the end we shall restrict ourself to the one dimensional system which is the purpose of the present paper.

V. The 1d Quartic Approximation

Let us expand the pair interactions up to the fifth order:

$$f(r_i - r_j) = \sum_{l=0}^{5} f_l^{ij} \frac{(q_i - q_j)^l}{l!} \tag{27}$$

with

$$f_l^{ij} = \partial^l f/\partial r^l \quad \text{taken for} \quad r = R_i - R_j = (i-j)\,\boldsymbol{a}\,, \tag{28}$$

which gives also, for this fundamental state of this perfect crystal,

$$f_l^{ij} \equiv f_l^{0(j-i)}, \quad K(q) = \sum_{l=0}^{5} K_l \frac{q^l}{l!}\,, \tag{29}$$

with

$$K_l = \sum_{n \neq 0} f_l^{0n}\,. \tag{30}$$

These last constants (versus q, but functions of the lattice parameter $\boldsymbol{a}$) are non-zero only for even l's, if the interaction f depends only upon the absolute value of r (isotropic interaction).

Similarly we expand the density function:

$$u(q) = \sum_{l=0}^{5} u_l \frac{q^l}{l!}\,. \tag{31}$$

Solving (5) using (23) and (24) one gets for $l \geq 1$:

$$u_l = (-)^l \sum_{j \neq i} \sum_{m=0}^{5-l} f_{l+m}^{ij} \frac{\langle q^m \rangle}{m!}\,, \tag{32}$$

and for $l = 0$:

$$u_0 = \sum_{j \neq i} \sum_{m=0}^{l} f_{0m}^{ij} \frac{\langle q^m \rangle}{m!} - 1/2 \sum_{j \neq i} \sum\sum_{m,\,p \geq 0}^{m+p=5} f_{p+m}^{ij} \frac{\langle q^m \rangle}{m!} \frac{\langle q^p \rangle}{p!}\,, \tag{33}$$

or solving (6) using (25) and (26) one gets for $l \geq 1$:

$$u_l = (-)^l \sum_{m=0}^{5-l} K_{l+m} \frac{\langle q^m \rangle}{m!}, \tag{34}$$

and for $l=0$:

$$u_0 = \sum_{m=0}^{5} K_m \frac{\langle q^m \rangle}{m!} - 1/2 \sum\sum_{m,\, p \geq 0}^{m+p=5} K_{m+p} \frac{\langle q^m \rangle}{m!} \frac{\langle q^p \rangle}{p!}. \tag{35}$$

The summation can be restricted to 4 in the case of an isotropic interaction, as even terms of K are then *zero*; in that case $\langle q^m \rangle$ and u_m are also *zero* for odd m's.

One finds the self-consistent potential

$$u(q) = K_0/2 + K_2 q^2/2 + K_4 (q^4/24 + q^2 \langle q^2 \rangle/4 - \langle q^2 \rangle^2/8). \tag{36}$$

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

$$K_0^{\text{eff}} = K_0/2 - K_4 \langle q^2 \rangle^2/8 \tag{37}$$

and an effective curvature

$$K_2^{\text{eff}} = K_2 + K_4 \langle q^2 \rangle/2. \tag{38}$$

We ask now for the self-consistency of $\langle q^2 \rangle$, i.e., after eliminating some constants

$$\langle q^2 \rangle = \frac{\int \mathrm{d}q\, q^2 \exp\{-[K_4 q^4/24 + (K_4 \langle q^2 \rangle/4 + K_2/2) q^2]/\theta\}}{\int \mathrm{d}q \exp\{-[K_4 q^4/24 + (K_4 \langle q^2 \rangle/4 + K_2/2) q^2]/\theta\}}. \tag{39}$$

The constant K_4 has to be positive, otherwise the potential would be infinitely negative for infinite q, and our theoretical crystal would break or, better said, evaporate. This fact is coherent with the integrals in (33) becoming infinite for t imaginary.

If we write

$$t = q^2 \sqrt{\frac{K_4}{12\theta}} \quad \text{and} \quad y = (K_4 \langle q^2 \rangle/2 + K_2) \sqrt{\frac{3}{K_4 \theta}} \tag{40}$$

we can express the integrals

$$\int \mathrm{d}q\, q^{2p} \exp\{-u(q)/\theta\}$$

in terms of parabolic cylinder functions $\mathscr{D}$ (see the appendix):

$$\int \mathrm{d}q\, q^{2p} \exp\{-u(q)/\theta\}$$
$$= \exp\{(-K_0/2 + K_4 \langle q^2 \rangle^2 - y^2/4)/\theta\} \cdot \{12\theta/K_4)^{p/2+1/4}\, \Gamma(p+1/2) \mathscr{D}_{-p-1/2}\, y\}.$$

So, (39) could be written as

$$\sqrt{\frac{K_4}{12\theta}} \langle q^2 \rangle = \frac{\Gamma(1/2)\, \mathscr{D}_{-1.5}(y)}{\Gamma(-1/2)\, \mathscr{D}_{-0.5}(y)}. \tag{41}$$

Let us now introduce:

- a parameter $1/X$ measuring the relative strength of the quartic term relatively to the harmonic part of the interaction potential and to the temperature

$$X = K_2 \sqrt{3/(K_4 \theta)}, \tag{42}$$

- a normalized moment of order 2

$$\mathscr{S}_1 = \sqrt{\frac{K_4}{3\theta}} \langle q^2 \rangle. \tag{43}$$

Then

$$\mathscr{S}_1(y) = \frac{\mathscr{D}_{-1.5}(y)}{\mathscr{D}_{-0.5}(y)} \tag{44}$$

with

$$y = X + 3/2\, \mathscr{S}_1(X). \tag{45}$$

The normalized moment of order 2, $\mathscr{S}_1$, *is a universal function of the normalized quartic strength* $1/X$ by the implicit equation (see the appendix)

$$\mathscr{S}_1(X) = \frac{\mathscr{D}_{-1.5}[X + 3/2\, \mathscr{S}_1(X)]}{\mathscr{D}_{-0.5}[X + 3/2\, \mathscr{S}_1(X)]}. \tag{46}$$

Other moments are then

$$\langle q^{2p} \rangle = \frac{\Gamma(p+0.5)}{\Gamma(0.5)} (12\theta/K_4)^{p/2} \frac{\mathscr{D}_{-p-1/2}[X + 3/2\, \mathscr{S}_1(X)]}{\mathscr{D}_{-1/2}[X + 3/2\, \mathscr{S}_1(X)]}, \tag{47}$$

where the last quotient is a function of $\mathscr{S}_1(X)$ through the recursion

$$\langle q^{2p} \rangle = 2(3\theta/K_4)^{1/2} [(2p-3)(3\theta/K_4)^{1/2} \langle q^{2(p-2)} \rangle - y \langle q^{2(p-1)} \rangle], \tag{48}$$

established from the recursion relations on the parabolic cylinder functions recalled in the appendix.

The partial partition function (13) is

$$\boldsymbol{Z}_0^{1/N} = \boldsymbol{Z}(\theta, \boldsymbol{a}) = \{12\theta\pi^2/K_4\}^{1/4} \{2\pi m\theta/h^2\}^{1/2} \cdot \exp\{-[K_0/2 + K_4 \langle q^2 \rangle^2/8]/\theta + y^2/4\}\, \mathscr{D}_{-1/2}(y). \tag{49}$$

The non-improved free energy (16) is

$$F_0 = N\theta[K_0/2\theta - 3\mathscr{S}_1^2(X)/8 - y^2/4 - 1/4 \ln\{12\theta\pi^2/K_4\} - 1/2 \ln\{2\pi m\theta/h^2\} - \ln\{\mathscr{D}_{-1/2}(y)\}] \tag{50}$$

{recall that y is a function of X through (46)}.

Using the derivatives of X

$$\partial X/\partial \boldsymbol{a} = X\left(\frac{1\,\mathrm{d}K_2}{K_2\,\mathrm{d}\boldsymbol{a}} - \frac{1\,\mathrm{d}K_4}{2K_4\,\mathrm{d}\boldsymbol{a}}\right), \quad \partial X/\partial\theta = -X/(2\theta)\,, \tag{51}$$

the energy is, from (16):

$$E_0 = N/2\,[K_0 + \theta\{3 + X\mathscr{S}_1(X)\}/2]\,. \tag{52}$$

This formula can be written

$$E_0 = N\,[K_0/2 + 3\theta/4 + K_2\langle q^2\rangle/4]\,, \tag{53}$$

a very curious and simple result which does not explicitly include K_4 (the effect of which is buried in the mean second moment $\langle q^2\rangle$) and is different from the harmonic expression

$$E_0 = N[K_0/2 + \theta/2 + K_2\langle q^2\rangle/2]\,. \tag{54}$$

Then the molecular heat capacity at constant length is given by

$$C_{0\boldsymbol{a}} = k_\mathrm{B}/4\{3 + XS_1(X)/2 - X^2/2\,\mathrm{d}S_1/\mathrm{d}X\}\,, \tag{55}$$

and the one-dimensional "pressure", from (21):

$$A_0 = -\,1/2\,[\mathrm{d}K_0/\mathrm{d}\boldsymbol{a} + X\mathscr{S}_1(X)\,\theta\,\mathrm{d}(\ln K_2)/\mathrm{d}\boldsymbol{a} + \theta\{1 - X\mathscr{S}_1(X)\}\,\mathrm{d}(\ln K_4)/\mathrm{d}\boldsymbol{a}/2]\,. \tag{56}$$

Quantum corrections are

$$F_\mathrm{Q} = \frac{h^2 K_2}{96\pi^2\theta^2 m}(1 + 3S_1/X), \tag{50 bis}$$

$$E_\mathrm{Q} = \frac{h^2 K_2}{64\pi^2\theta m}(\mathrm{d}S_1/\mathrm{d}X + 3S_1/X + 4/3)\,, \tag{52 bis}$$

$$C_{\mathrm{Q}\boldsymbol{a}} = -k_\mathrm{B}\frac{h^2 K_2}{128\pi^2\theta^2 m}\left(\frac{X\,\mathrm{d}^2S_1}{\mathrm{d}X^2} + \frac{5\,\mathrm{d}S_1}{\mathrm{d}X} + \frac{3S_1}{X} + \frac{8}{3}\right), \tag{55 bis}$$

$$A_\mathrm{Q} = \frac{h^2 K_2}{96\pi^2\theta^2 m}\left[-\left(1 + 3\frac{\mathrm{d}S_1}{\mathrm{d}X}\right)\frac{\mathrm{d}K_2}{\mathrm{d}\boldsymbol{a}} + \frac{3K_2}{2K_4}\left(\frac{\mathrm{d}S_1}{\mathrm{d}X} - \frac{S_1}{X}\right)\frac{\mathrm{d}K_4}{\mathrm{d}\boldsymbol{a}}\right]. \tag{56 bis}$$

VI. Weak Anharmonicity

The interatomic distance $\boldsymbol{a}$ can be obtained by equating this last expression to a known external pressure, e.g. zero, a good approximation in many cases:

$$A_0 = 0\,. \tag{57}$$

Here we shall use this equation of state by starting at zero K, where classically the lattice parameter is r_0, the interatomic distance at the minimum of the interatomic potential, i.e. we write

$$\delta\boldsymbol{a} = \boldsymbol{a} - r_0\,.$$

Taking into account only nearest neighbour interactions in the un-improved approximation and expanding the force parameters K_0, K_2 and K_4 to the second order in $\delta\boldsymbol{a}$ around the zero Kelvin equilibrium value r_0 we have, to the second order in θ:

$$\begin{aligned}\delta\boldsymbol{a} = &-\frac{\theta}{2A}\left(\frac{\mathscr{S}_1XB}{A} + \frac{(1-\mathscr{S}_1X)\,D}{2C}\right)\\ &+\frac{\theta^2}{4A^4}\mathscr{S}_1^2X^2\left(C - \frac{3B^2}{2A}\right)B\\ &+\frac{(1-\mathscr{S}_1X)\,\theta^2}{4A^3}\left(\frac{D}{2B} - \frac{BC}{AD} - \frac{D^2}{2C^2}\right)B\\ &-\frac{\theta^2}{4A^2}\left(\frac{1-\mathscr{S}_1X}{4}\right)^2\frac{D^2}{C^2}\left(\frac{D}{C} + \frac{B}{2A}\right),\end{aligned} \tag{58}$$

where

$$A = f_2(r_0), \quad B = f_3(r_0), \quad C = f_4(r_0), \quad D = f_5(r_0)\,. \tag{59}$$

In the case of the noncorrelative approximation at weak anharmonicity, i.e. when

$$X \to \infty\,,$$

then

$$\mathscr{S}_1 \to 1/X - 3/X^2 + 39/(2X^4)\,,$$

the Helmholtz free energy is

$$F_0 = N\left\{-\frac{\theta}{2}\ln\left(\frac{4\pi^2 m\theta}{K_2 h^2}\right) + \frac{K_0}{2} - \frac{K_4\theta^2}{4K_2} + \frac{13K_4^2\theta^3}{48K_2^4}\right\}, \tag{60}$$

the energy is

$$E = N\left(\theta + \frac{K_0}{2} - \frac{K_4\theta^2}{4K_2^2} + \frac{13K_4^2\theta^3}{24K_2^4}\right), \tag{61}$$

and the moments of the position are

$$\langle q^2\rangle = \frac{\theta}{K_2}\left(1 - \frac{K_4\theta}{K_2^2} + \frac{13K_4^2\theta^2}{6K_2^4} - \frac{25K_4^3\theta^3}{4K_2^6}\right), \tag{62}$$

$$\langle q^4\rangle = \frac{3\theta^2}{K_2^2}\left(1 - \frac{7K_4\theta}{3K_2^2} + \frac{43K_4^2\theta^2}{6K_2^4}\right), \tag{63}$$

$$\langle q^6\rangle = \frac{15\theta^3}{K_2^3}\left(1 - \frac{4K_4\theta}{K_2^2}\right), \tag{64}$$

$$\langle q^8\rangle = \frac{105\theta^4}{K_2^4}\,. \tag{65}$$

The thermal expansion is given by

$$\delta \boldsymbol{a} = -\frac{\theta B}{2A^2}\left(1+\frac{\theta}{A^2}\left(\frac{3B^2}{4A}-C+\frac{AD}{4B}\right)\right), \quad (66)$$

the molecular heat capacity at constant length is

$$C_{0a} = R\left(1-\frac{K_4\theta}{2K_2^2}+\frac{13K_4^2\theta^2}{8K_2^4}\right), \quad (67)$$

R being the gas constant.

If

$$C \ll A/r_0^2,$$

then we can be confident in the linear approximation in temperature

$$\langle q^2\rangle = \theta/\{2A\}, \quad (68)$$

which does not include neither the cubic term or any odd terms, nor the quartic term. So, the expression for the thermal expansion δa takes the form given in [7]

$$\delta \boldsymbol{a} = -\theta B/(2A^2). \quad (69)$$

In this approximation, (14) to (16) coincide with the Einstein harmonic approximation.

Using the approximation (68) and taking into account weak anharmonicity at moderate temperature, (56) leads to the same formula as obtained in [11]:

$$\delta \boldsymbol{a} = -\theta B/(2A^2)\,[1+\theta/A^2\{3B^2/(4A)-C+AD/(4B)\}]. \quad (70)$$

So, (70) can be obtained using two assumptions: weak anharmonicity in relation to the self-consistent potential, and harmonic approximation in relation to the effective amplitudes of an infinite linear chain.

Note that the temperature-dependent part of the effective depth of the crystal field given in (37)

$$-\theta^2 C/(16A^2),$$

is, as long as it is smaller, much greater than the correction due to the thermal expansion

$$(\theta^2 C/(16A^2))^2/(64A),$$

which is too often only considered.

Here it must be mentioned that the Helmholtz free energy calculated in the quasi-harmonic approximation of the unsymmetrized self-consistent field method for 1d systems can be obtained directly from (60) by assuming that

$$\frac{K_4\theta^2}{4K_2} \ll 1 \quad (71)$$

and can be neglected. So, in the quasi-harmonic approximation we find that

$$F_0 = N\left\{-\ln\theta - \frac{1}{2}\ln\left(\frac{4\pi^2 m}{K_2 h^2}\right)+\frac{K_0}{2}\right\}. \quad (72)$$

Thus the energy and pressure take the form

$$E_0 = N\left(\theta+\frac{K_0}{2}\right), \quad (73)$$

$$A_0 = -1/2\,[\mathrm{d}K_0/\mathrm{d}\boldsymbol{a} + \theta\,\mathrm{d}(\ln K_2)/\mathrm{d}\boldsymbol{a}]. \quad (74)$$

This approximation gives the Dulong and Petit law and the Mie-Grüneisen-Type equation of state.

VII. Approximate Approach

Let us assume that $K_4\theta < 3(K_2)^2$. Then the integrals of the form

$$\int \mathrm{d}q\, q^{2p} \exp\{-u(q)/\theta\}$$

can be expanded in Taylor series in powers of $(K_4 q^4/24\theta)$:

$$\int \mathrm{d}q\, q^{2p} \exp\{-u(q)/\theta\} = \sqrt{2\pi}\exp\left(-\frac{u_0}{\theta}\right)\left(\frac{\theta}{u_2}\right)^{(p+0.5)} \cdot \sum_{i=0}^{\infty}\frac{(-1)^i}{i!}\left(\frac{1}{u_2}\sqrt{\frac{\theta K_4}{3}}\right)2i\,\frac{(2p+4i-1)!!}{2^{3i}}, \quad (75)$$

where (see (34))

$$u_2 = K_2 + 0.5\,K_4\langle q^2\rangle.$$

So, by taking into consideration that $y = u_2\sqrt{3/\theta K_4}$ (see (40)) the moment $\langle q^2\rangle$ of the distribution function $w(q)$ could be written as

$$\langle q^2\rangle = \sqrt{\frac{3\theta}{K_4}}\,\frac{\left(\sum_{i=0}^{\infty}\frac{(-1)^i}{i!}\,y^{-(2i+1)}\,\frac{(4+4i-1)!!}{2^{3i}}\right)}{\left(\sum_{i=0}^{\infty}\frac{(-1)^i}{i!}\,y^{-2i}\,\frac{(4i-1)!!}{2^{3i}}\right)}. \quad (76)$$

Equation (76) is not linear in relation to $\langle q^2\rangle$, but it could be solved by successive approximations starting directly from the harmonic approximation for $\langle q^2\rangle$ in y

$$\langle q^2\rangle = \frac{\theta}{K_2}. \quad (77)$$

This means that we start by putting

$$y = X + \frac{3}{2X} \quad (45\,\text{bis})$$

with $X = K_2\sqrt{3/(K_4\theta)}$ (see (42)).

This procedure allows $\langle q^2 \rangle$ to be expressed in a series of the form

$$\langle q^2 \rangle = \sqrt{\frac{3\theta}{K_4}} \left(1 - \frac{3}{X^2} + \frac{39}{2X^4} - \frac{675}{4X^6} + \frac{13\,869}{8X^8} - \frac{323\;757}{16X^{10}} + \frac{8\,424\,027}{32X^{12}} + \frac{3\,786\,880}{X^{14}} + \ldots\right) \tag{78}$$

when $K_2 > 0$, or of the form

$$\langle q^2 \rangle = \frac{3\theta K_2}{K_4} \left(-\frac{X}{2} + \frac{1}{X} + \frac{18}{X^3} + \frac{1\,032}{X^5} + \frac{98\,280}{X^7} + \frac{12\,842\,208}{X^9} + \frac{2\,110\,163 \cdot 10^3}{X^{11}} + \frac{4\,154\,197 \cdot 10^5}{X^{13}} + \frac{9\,505\,437 \cdot 10^7}{X^{15}} + \ldots\right) \tag{79}$$

when $K_2 < 0$.

The series (78) and (79) are diverging, but one can circumvent this difficulty through the use of the ε-algorithm [9–11]. Then, if we introduce the function $\mathscr{S}_{1,\varepsilon}$ defined by

$$\mathscr{S}_{1,\varepsilon} = \frac{\langle q^2 \rangle}{\sqrt{3\theta/K_4}}, \tag{80}$$

the application of this approach to calculate the termodynamic properties of crystal leads to the same formulae (49)–(56) but $\mathscr{S}_1$ should be replaced by $\mathscr{S}_{1,\varepsilon}$.

The calculation of $\mathscr{S}_1(X)$ and $\mathscr{S}_{1,\varepsilon}(X)$ is demonstrated in Fig. 1, where we see that there is no practical difference between these two functions when $X > 0$ (i.e. $K_2 > 0$), while the difference between them is important when $X < -1$ (i.e. $K_2 < 0$). So, the approximate approach could be applied with a very good precision when we deal with an interaction potential which has a positive second derivative (this is the case for the Lennard-Jones central pairwise potential). This approach, as well as the precise one, can be used to calculate the correlation and quantum corrections and also to include higher order terms of the interaction potential.

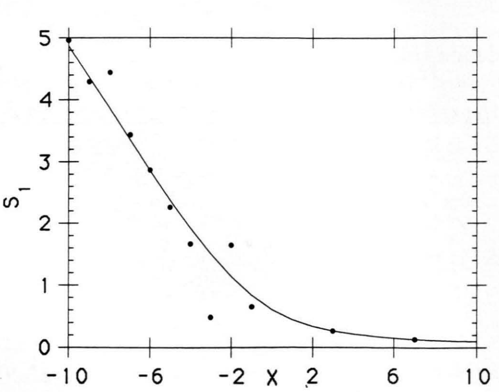

Fig. 1. The S_1 (——) and $S_{1,\varepsilon}$ (●) functions.

Here it should be mentioned that this approach is valid only when $|X| > 1$.

VIII. Conclusion

We have verified that the quantum correction to the specific heat

$$\frac{-h^2 K^2}{24\pi^2 m\,kT^2}$$

is the low temperature first term of the exact phonon theory restricted to harmonic interaction (and not of the Debye approximation which we calculated to be by $\pi^2/6$ larger for the linear chain); i.e. phonons with small wavelength, reflecting the correlations at small distance only, are well taken into account.

Comparisons to the phonon theory with higher potential terms [12] shows reasonable agreement if one includes the first term of the correlation correction.

We calculated the thermal expansion and the specific heat for a linear chain of argon, where the five first terms of the expansion of the potentiel were taken from the Lennard-Jones effective 6–12 potentiel for ordinary 3d krypton, [13] discussed in [14]. We show the calculations of the thermal expansion (Fig. 2) based on different numbers of terms in the series (78), on the ε-algorithm, [3], [5] and the on the $\mathscr{S}_1$ function. In Fig. 3 we show the specific heat with and without quantum corrections.

In summary, the use of the S_1 function enables one to calculate exactly the properties of a linear chain of atoms with quartic interactions. Comparing them to different kinds of expansions, one can appreciate the range of validity of these expansions. The expansion of $\langle q^2 \rangle$ for small anharmonicities or high temperatures ($X \to \infty$) is diverging. One is then not surprised 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. One can circumvent this difficulty through the use of the ε-algorithm: the range of validity grows then with the order of approximation and can be much extended.

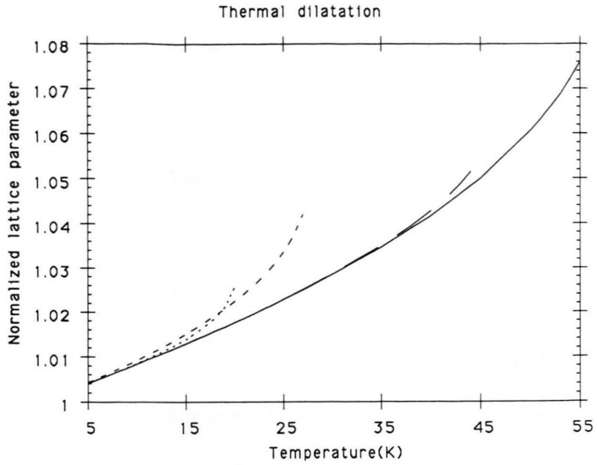

Fig. 2. Thermal classical dilatation for 2d argon calculated using the S_1 function (——), the quasi-harmonic approximation (– – –), first three terms of series (· · · ·) and $S_{1,\varepsilon}$ function (— —).

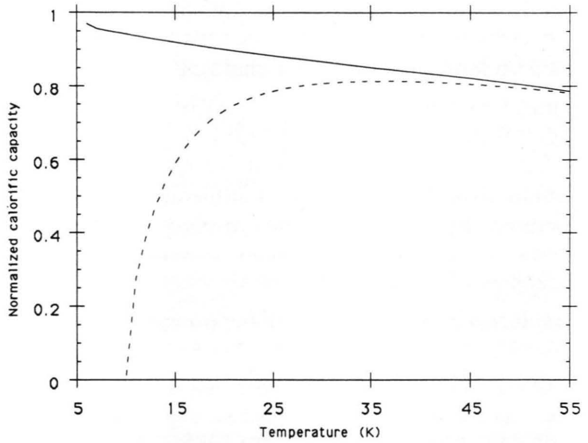

Fig. 3. Calorific capacity (in R units) with (– – –) and without (——) quantum corrections for 2d argon.

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Appendix: The Function $\mathscr{S}_1$

We use the parabolic cylinder functions defined in § 16.6 of [15]

$$\mathscr{D}_n(z) = -\exp\{-z^2/4\}\,\Gamma(n+1)/(2i\pi) \cdot \int_{\infty}^{(0+)} \frac{\exp\{-t^2/2 - z\cdot t\}\,\mathrm{d}t}{(-t)^{n+1}} \tag{A.1}$$

from which we derive for $n > 0$, see also [16]:

$$\mathscr{D}_n(y) = \exp\{-y^2/4\}/\Gamma(-n) \int_0^{\infty} \frac{\exp\{-t^2/2 - y\cdot t\}\,\mathrm{d}t}{t^{n+1}}, \tag{A.2}$$

using also (for non-integer n)

$$\Gamma(-n)\,\Gamma(n+1)\sin\big(\pi(n+1)\big) = \pi\,.$$

By doing the change of variables (40)

$$t = q^2\sqrt{\frac{K_4}{12\theta}} \quad \text{and} \quad y = (K_2 + K_4 q^2/2)\sqrt{\frac{3}{K_4\theta}}\,,$$

we transform

$$I_{2p} = \int_{-\infty}^{\infty} \mathrm{d}q\, q^{2p} \exp\{-u(q)/\theta\}\,,$$

where (36)

$$u(q) = K_0 + K_2 q^2/2 + K_4\{\langle q^2\rangle q^2/4 + q^4/24 - \langle q^2\rangle^2/8\}$$

to

$$I_{2p} = \left(\frac{K_4}{12\theta}\right)^{-p/2-1/4} \Gamma(p+1/2) \cdot \exp\{-K_0/2 + K_4\langle q^2\rangle/8\}\exp\{-y^2/4\}\,\mathscr{D}_{-p-1/2}(y). \tag{A.3}$$

Then (47)

$$\langle q^{2p}\rangle = \frac{\Gamma(p+1/2)}{\Gamma(1/2)}\left(\frac{K_4}{12\theta}\right)^{-p/2} \frac{\mathscr{D}_{-p-1/2}(y)}{\mathscr{D}_{-1/2}(y)}, \tag{A.4}$$

and

$$z(\theta) = I_0 = \left(\frac{K_4}{12\theta}\right)^{-1/4} \sqrt{\pi}\exp\{-K_0/2 + K_4\langle q^2\rangle/8\} \cdot \exp\{-y^2/4\}\,\mathscr{D}_{-1/2}(y) \tag{A.5}$$

We define the function $\mathscr{S}_1(x)$ by:

$$\mathscr{S}_1(x) = \frac{\mathscr{D}_{-1.5}(y)}{\mathscr{D}_{-0.5}(y)} = 2\,\frac{K(y)}{L(y)} \tag{A.6}$$

with

$$y = x + 3/2\, S_1(x)\,, \tag{A.7}$$

$$K(y) = \int_0^{\infty} \sqrt{t}\exp\{-t^2/2 - y\cdot t\}\,\mathrm{d}t\,, \tag{A.8}$$

and

$$L(y) = \int_0^{\infty} \frac{\exp\{-t^2/2 - y\cdot t\}}{\sqrt{t}}\,\mathrm{d}t\,. \tag{A.9}$$

Taking the derivative of K and L with respect to y and integrating L by parts, which gives

$$\mathrm{d}L/\mathrm{d}y = -K\,, \tag{A.10}$$

$$\mathrm{d}K/\mathrm{d}y = yK - L/2\,, \tag{A.10bis}$$

or using the following relations for parabolic cyclinder functions, see § 16.61 in [15] or [16]:

$$\mathscr{D}_{n+1}(y) - y\mathscr{D}_n(y) + n\mathscr{D}_{n-1}(y) = 0\,,$$

$$\mathscr{D}'_n(y) + y\mathscr{D}_n(y)/2 - n\mathscr{D}_{n-1}(y) = 0\,,$$

we find

$$\mathrm{d}\mathscr{S}_1(x)/\mathrm{d}y = \mathscr{S}_1(x)^2/2 + \mathscr{S}_1(x)\,y - 1\,, \tag{A.11}$$

and we arrive at the first order differential equation for $\mathscr{S}_1$

$$\mathrm{d}\mathscr{S}_1/\mathrm{d}x = \frac{-1 + x\mathscr{S}_1 + 2\mathscr{S}_1^2}{2.5 - 3x\mathscr{S}_1/2 - 3\mathscr{S}_1^2} \tag{A.12}$$

which we shall integrate using its asymptotic value for $x \to \infty$.

A remarkable value is obtained for $y=0$, i.e. for $x = -3\mathscr{S}_1/2$; from

$$\Gamma(x) = \mu^{-n} \int_0^\infty x^{n-1} \exp(-\mu x)\,\mathrm{d}x$$

and the transformation $x = t^2/2$, we find

$$K(0) = 2^{-1/4}\,\Gamma(3/4)\,,$$

$$L(0) = 2^{-3/4}\,\Gamma(1/4)\,,$$

for $y = 0$

$$\mathscr{S}_1 = 2\sqrt{2}\,\frac{\Gamma(7/4)/(3/4)}{\Gamma(5/4)/(1/4)} = 2\sqrt{2}\cdot 0.9191/0.9064/3 = 0.9760_2$$

from the tables [17], p. 364. We shall verify that

$$\mathscr{S}_1(-1.454) = 0.9760\,.$$

We give in Fig. 1 the curve representing this calculation of S_1 from $x = -10$ to $x = 10$.

Using the asymptotic expansion of $\mathscr{D}_n(y)$, § 16.5 in [17],

$$\mathscr{D}_n(y) = \exp(-y^2/4)\,y^n \left(1 - \frac{n(n-1)}{2y^2} + \frac{n(n-1)(n-2)(n-3)}{2\cdot 4\cdot y^4} - \frac{n(n-1)(n-2)(n-3)(n-4)(n-5)}{2\cdot 4\cdot 6\cdot y^6} + \frac{n(n-1)(n-2)(n-3)(n-4)(n-5)(n-6)(n-7)}{2\cdot 4\cdot 6\cdot 8\cdot y^8} + \ldots\right), \tag{A.13}$$

when

$$y \Rightarrow +\infty, \quad -3\pi/4 < \mathrm{Arg}(y) < 3\pi/4$$

it is easy to find the first terms of the asymptotic expansion for $x \to \infty$:

$$\mathscr{S}_1 \Rightarrow \frac{1}{x}\left(1 - \frac{3}{x^2} + \ldots\right). \tag{A.14}$$

From the asymptotic expansion (§ 16.52 in [15]) for

$$y \Rightarrow -\infty; \quad \pi/4 < \mathrm{Arg}(y) < 5\pi/4$$

we extract for y negative and real

$$\mathscr{D}_n(y) = \frac{\sqrt{2\pi}}{\Gamma(-n)} \exp(+y^2/4)(-y)^{-n-1} \left\{1 + \frac{n(n+1)}{2y^2} + \frac{n(n+1)(n+2)(n+3)}{2\cdot 4\cdot y^4} + \frac{n(n+1)(n+2)(n+3)(n+4)}{2\cdot 4\cdot y^6} + \frac{n(n+1)(n+2)(n+3)(n+4)(n+5)(n+6)}{2\cdot 4\cdot 6\cdot 8\cdot y^8} + \ldots\right\}.$$

With the same procedure as for x positive we get the asymptotic expansion for $x \to -\infty$

$$\mathscr{S}_1 \Rightarrow -\frac{x}{2} + \frac{1}{x} + \frac{18}{x^3} + \ldots\,. \tag{A.15}$$

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