

Theoretical calculation of equations of state: analytical results

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Abstract. Rigorous, analytical first-principle equation-of-state results derived at the VNIIEF from exact approaches are reviewed in detail.

1. Introduction

This review was prepared in connection with the 50th anniversary of the All-Russian Scientific Research Institute of Experimental Physics (VNIIEF, 1946–1996). Almost all this time (1946–1992) the institute was under the scientific direction of Yu B Khariton, physicist and intellectual, a man of exquisite culture, ethical principles and tact, hardworking and modest in everything, and always approachable for everyone. I discussed many issues with Yu B Khariton and this work in particular, and he immediately approved of its expedience. For this review I selected mainly the results on the theoretical calculations of the equation of state (EOS) of

crystalline solids, obtained over the years in the departments of G M Gandel'man and N A Dmitriev of the Division of theoretical physics of VNIIEF (headed by Yu A Trutnev), carried through to exact analytical expressions. Such results do not grow obsolete, and therefore will be interesting and useful both scientifically and methodologically for anyone who is studying or working in this field or related disciplines: students and postgraduate, teachers, young researchers, who make up a considerable proportion of UFN's readership. A glance at the table of contents will give a good notion of the selection of rigorous analytical results that we are going to present to the reader — in a self-consistent manner and in sufficient detail. Such a self-contained presentation is designed to facilitate understanding of analytical results (which are unavoidable and essential in a review of this kind). We tried to make the material as digestible as possible, and to provide easy and useful reading.

2. Brief review of the main approaches to calculation of the equation of state

2.1 History of the problem

One of the main tasks of the theory of systems of many interacting particles is to explain the observed properties of macroscopic bodies from the known forces between the component particles — nuclei (ions) and electrons; that is, from the model microscopic calculations. These are not necessarily calculations from first principles. Compare, for

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example, the calculation of steady states of the atom and calculation of its nucleus. The former can be accomplished from first principles, because we know the exact law of electromagnetic interactions. The latter, however, even though microscopic, is not a calculation from first principles, because the exact law of interaction between nucleons is not known. It is this situation that is encountered in the calculations of *substances*, if the structural units in the macroscopic model of matter are whole atoms or molecules: although the nature of forces between them is known (it is electromagnetic), the governing law is not. The simple law of Coulombian interaction of electrons and nuclei of atoms or molecules works here in many complex and diverse ways: attraction, repulsion, saturation of chemical forces, directional chemical valences, etc. In this review we have included theoretical calculations concerned mainly with solid crystals and based on first principles. In other words, the structural units of the model are not the atoms (or molecules), but the nuclei and electrons of the crystal.

The approach relying on first principles and based on strictly quantum mechanical (or quantum statistical) calculation of *pressure* in crystal was started in the late 1950s in the Division of theoretical physics of VNIIEF by G M Gandel'man and N A Dmitriev, joined later (in 1967) by the author of this review. My collaboration with G M Gandel'man and N A Dmitriev, and later with N A Dmitriev continued for more than 20 years, and this review essentially is a systematic and detailed presentation of analytical results on the EOS of crystal, obtained by G M Gandel'man, N A Dmitriev and myself (some numerical calculations based on these theoretical conclusions were published in Refs [1–8]; they are left out of this review because they all were done in specific approximations). The idea of such a review was discussed at length with N A Dmitriev¹, who thought highly of it, but for a number of reasons he was not able to take part in the work. From conception, the work was not supposed to examine in detail the entire diversity of other approaches to the solution of the same problem, which, incidentally, are of the one-particle nature from the start.

By way of illustration we might mention semi-phenomenological [9, 10], Thomas–Fermi (TF) [11, 12], quasi-classical (with and without various corrections) [13, 14] schemes, as well as more substantial but still one-particle approaches, such as the methods of attached plane waves (APW) [15] and attached spherical waves (ASW) [16], the theory of the density functional (TDF) [17, 18], the method of Corringi–Cohn–Rostocker (CCR) [19, 20], and, finally, various simplifications of the Hartree–Fock (HF) approximation [21–23]. Out of the many-particle approaches to the problem of strongly compressed matter we ought to mention those presented in Refs [24, 25]. As a matter of fact, the decision to delimit the scope of the review was made for three reasons. Firstly, this review is a kind of a jubilee report in celebration of the 50th anniversary of VNIIEF. Secondly, a detailed review would require much more space than is available (see, for example, a substantial even if not too recent review in Ref. [26]). Thirdly, I, an alumnus of the department of physics of Moscow State University, and an adherent of the scientific principles of

N A Dmitriev², favor approaches based on first principles, even though they are always less spectacular (in the sense of the shortcut to the boon of a numerical result) than the asymptotic approaches that are always much simpler from both mathematical and technical standpoints. Of course, simplicity (not to be confused with primitivity), according to ancient Greeks, is usually a mark of truth. It is not that easy to formulate a physical problem in a simple way while retaining all of its essential features.

2.2 Specifics of one-particle calculations of pressure

The analytical calculation of the EOS of matter used to begin (and still does) with the calculation of the internal or free energy in the one-particle approximation. Unlike that, G M Gandel'man and N A Dmitriev, independently off each other, took the path of direct calculation of the pressure in matter — to be more precise, in crystal — aiming at the exact quantum mechanical or quantum statistical expressions. In the case of the one-particle approach one immediately has to deal with such entities as the exchange energy and the correlation energy that are not encountered in the exact many-particle statement. Because of this, the initial one-particle expressions for the free energy of the cell or even for its electron part have to be put together from separate pieces, often relating to different approximations and so, as a rule, not admitting of a reliable internal check. The most consistent and rational of the one-particle approximations is apparently the purely quantum mechanical HF method. Unfortunately, this method does not take into account the dynamic correlation of the electrons of matter, although the exchange is taken into account in a rigorous way. An attempt at finding a compromise solution of this problem is the Cohn–Sham scheme for expressing the set of self-consistent one-particle equations [17] based on the simultaneous semi-quantitative inclusion of exchange and correlation. In practice, this scheme as a rule gives better results than even the sophisticated calculations by the HF technique (when it comes to the calculation of physical properties of small systems). These schemes, however, are extremely laborious. Somewhat simpler than the HF method are the Hartree model and the modified HF method. In the former case the exchange part of the potential of the HF approximation is totally disregarded, while in the modified HF scheme this part of the potential, which in the exact HF model is non-localized, is replaced with a simple function of the coordinate (Slater [27]). The simplest of all is the statistical Thomas–Fermi (TF) method, which completely disregards the existence of the cell structure (incidentally, it is this method that was used in Ref. [12] in an attempt to take the cell structure into account; this problem was later treated in Refs [28–30]). The TF method is based on the simultaneous application of classical electrostatics (for calculation of the potential in the cell) and the Pauli principle for occupation of the one-electron states of the cell. The inclusion of the cell structure into consideration would have been an unreasonable luxury for this approxima-

¹ G M Gandel'man was no longer with us, and I could not benefit from his advice, the advice of a person of most powerful physical intuition — this is how I see him in my mind's eye.

² N A Dmitriev was a mathematician by education (a graduate of the department of mathematics of Moscow State), an analyst by nature, and a physicist by the call of times (he was the right hand of Ya B Zel'dovich when they worked together on the nuclear project), one of the few strongest and most universal theoreticians of VNIIEF (ranking with Ya B Zel'dovich, A D Sakharov, D A Frank-Kamenetskii, K I Shchelkin), and perhaps the best versed in analytical and computational techniques. See memoir on p. 1015.

tion. As a matter of fact, in crystals with high symmetry (cubic, for example) the cell also has high symmetry, and can therefore be regarded as a sphere of the same volume, with spherical boundary conditions. In practice, however, the actual non-isolatedness of the cell is represented by the value of its radius, which is selected from the given density of matter. In this way, the initial problem is reduced to the calculation of properties of one completely isolated electrically neutral cell. It is important to note that the TF method has a very limited applicability to matter occurring under normal conditions, because it is not capable of explaining not only the periodical properties of elements (determined by the properties of the outer electron shells), but even the forces of cohesion in matter. If, however, the matter occurs under extremely high pressures or temperatures, which are sufficient for destroying the effects of the outer shells, then the TF method leads to quite reasonable physical results: at high densities the forces of repulsion (exponential) prevail over the forces of attraction (power-law), and at high temperatures the forces of cohesion can be totally neglected.

The problem of calculation of macroscopic properties of perfect crystals is usually solved with the aid of the Bloch model, which at once reduces the initial problem to the calculation of one-electron states of an individual electron in the field of a periodic effective crystal potential [31]:

$$\left[-\frac{\hbar^2 \Delta}{2m} + U_{\mathbf{k}n}(\mathbf{r}) \right] \psi_{\mathbf{k}n} = E_{\mathbf{k}n} \psi_{\mathbf{k}n}(\mathbf{r}). \quad (2.1)$$

Because the potential is periodic, the solution of this problem for an entire crystal reduces to solving the same problem for one electrically neutral cell with the appropriate boundary conditions on the surface of the cell. Bloch's conditions are usually selected in the form [31]

$$\psi_{\mathbf{k}n}(\mathbf{r} + \mathbf{R}) = \exp(i\mathbf{k}\mathbf{R}) \psi_{\mathbf{k}n}(\mathbf{r}), \quad (2.2)$$

where \mathbf{R} is an arbitrary vector of the crystal lattice. Accordingly, all theoretical calculations in this approximation are carried out for one cell of a simplified rather than actual form. An exact (although quite cumbersome) approach to the solution of the one-electron Bloch problem (2.1) in crystal is developed in Ref. [32]. We ought to mention also Ref. [33], which proposes an analytical method for calculating the partition function for the Hamiltonian of a one-particle problem like Eqn (2.1). Although the knowledge of the partition function (statistical sum) allows one to calculate all thermodynamic functions, the calculation of strictly quantum mechanical functions requires knowing the wave functions of the problem (2.1).

2.3 Specifics of direct calculation of pressure

The above methods of calculation of EOS belong to the type of one-particle approximations. In its exact statement, the initial many-particle problem does not reduce even to the many-electron calculation of just one cell of matter with Bloch's boundary conditions on its surface, because the actual instantaneous states of individual cells at any given time are different, and so the portrayal obtained by exact duplication of one given cell in the space with the boundary conditions defined on its surface does not represent the true instantaneous state of the entire crystal. All this follows analytically from the conventional Hamiltonian of the crystal: its stationary states are not necessarily such for

individual cells, since the operators relating to individual cells, generally speaking, do not commute with the Hamiltonian itself. Sometimes the steady state of one cell represents the steady state of the entire crystal; in this case, however, it will be a *static* state (for example, the Ising model).

For the first time, the many-particle exact direct calculation of pressure in the actual crystal cell with fixed nuclei was solved by Dmitriev [34]. His formula for pressure in crystal³ has a property very important for practical calculations: he eliminated from straightforward consideration the contribution to the kinetic part of the pressure from the internal (skeleton) electrons of the cell, and the strong intracell interaction between all electrons in the cell. His formula represents the pressure in the cell as an algebraic sum of two parts: the kinetic pressure of electrons expressed in terms of derivatives of the one-electron density matrix on the surface of the cell, and the Coulombian pressure related to the electrostatic interaction of cells only with one another. The electron part of the Coulombian pressure is expressed in terms of densities of electrons of the first and second orders.

Dmitriev's formula for the pressure in the crystal cell leads to the calculation of the difference $P_{\text{kin}} - |P_C|$ of two quantities that are of the same order of magnitude as the difference itself, whereas differentiation of the total energy of the ground state of the crystal with respect to its volume, or a straightforward application of the virial theorem (VT) (which, unfortunately, is often recommended; see, for example, Ref. [36], p. 61) leads to the calculation of a *small* difference of two *large* numbers, since even for a large compression force the change in the energy is small compared to its absolute magnitude. The same applies to the difference of quantities $E + E_{\text{kin}}$ and $2E_{\text{kin}} + E_{\text{pot}}$ ($E = E_{\text{kin}} + E_{\text{pot}}$) in the virial theorem: $3PV = 2E_{\text{kin}} + E_{\text{pot}}$.

Just a few months after the publication of Dmitriev's paper [34], a similar result was published by Gandel'man [1]; the two approaches, however, were not the same. Dmitriev used the classical method of virtual work, while Gandel'man used the quantum mechanical stress tensor. For a fair and comprehensive evaluation of the Dmitriev–Gandel'man formula it would be worthwhile comparing with the results of Liberman [37] and Janak [38].

The extension of Dmitriev's formula for cold pressure to the case of small but finite temperatures was derived by the author in Ref. [39]. Here the total pressure in crystal at finite temperatures is expressed via the temperature density matrices in the same way as the cold pressure in Dmitriev's formula. Actual calculations of the EOS of metals at our institute were done using the Dmitriev–Gandel'man formula, for the most part in the HF approximation for the ground state. In the first place this was due to the immense complexity and laboriousness of the task: it took several years to write and debug the program to obtain an acceptably self-consistent numerical solution of the HF equations⁴. Secondly, the true HF approximation (exact solution of the HF equations for a real crystal cell) is of extraordinary impor-

³ The analogue of Feynman's formula for a molecule: in Feynman's formula the forces between nuclei in the molecule are expressed in terms of its wave functions; the pressure in Dmitriev's formula is expressed via the density matrix.

⁴ This work was conducted in the Department for nonstandard problems of the Division of mathematics of VNIIEF (headed by I D Sofronov), with active and pivotal participation of the leader of this division V G Podval'nyi, who, regretfully, left us so early.

tance for the many-body problem, because, as we have demonstrated elsewhere [40], it remains the *zero* approximation for *any* reworks of the perturbation theory expansion. To evaluate the practicability of the HF approximation in the sense of its sufficiency we deemed it reasonable to find the correlation correction in the approximation of random phases. This problem was solved for the case of cold pressure in Ref. [4]. Calculations were done for vanadium.

2.4 Nature of compression

Generally speaking, the Hamiltonian of the system is a function of not only its volume Ω , but also its shape. Because of this, the correct application of the quantum mechanical operator of pressure $\hat{P} \equiv -\partial H/\partial \Omega$ (see also paragraph 1 of the Appendix) in calculations of EOS of matter requires taking due account of the manner in which the change of volume of the system has taken place. Indeed, since different directions in crystal are not equivalent, the analogue of, for instance, the isotherm of an ideal gas $PV = \text{const}$ is the linear tensor linkage between mechanical stress σ_{ik} and a small deformation u_{ik} of the crystal [41]:

$$\sigma_{ik} = Ku_{11}\delta_{ik} + 2\mu\left(u_{ik} - \frac{u_{11}\delta_{ik}}{3}\right). \quad (2.3)$$

Because of this, analytical simplifications of the EOS are usually based on two assumptions that allow circumvention of the problems arising from anisotropy of the crystal:

(a) the body is under all-around isotropic stress, and

(b) this stress results in a strain that is also isotropic: $\mathbf{R}' = (1 \pm \varepsilon)\mathbf{R}$ (generally speaking, such a state will not be an equilibrium one, but its energy will differ from the energy of the equilibrium state in the new volume by an infinitesimal of second order).

The second assumption may actually come true, and no more than approximately, for bodies with a high degree of internal symmetry, such as homogeneous amorphous substances, polycrystals, monocrystals with cubic symmetry, or when the compressed substance occurs in a liquid (molten) state. This is usually assumed in the analysis of strong shock compression of solids. Under these assumptions, the *elastic* properties of matter are described by just *one* parameter — the volume compressibility $-\partial\Omega/(\Omega\partial P)$, which is mainly determined by the electrons of matter, and the pressure is assumed to be of hydrostatic nature. With this approach to the calculation of EOS (that is, assuming the self-similar change of shape of the body), it is obviously not possible to describe phase transitions (PT) in crystal associated with the change of crystal lattice, and only those PT are described that are associated with the change in the electron configuration of atoms, and therefore with the change in the electron spectra of crystals (the so-called Fermi phase transitions [42]).

3. Quantum mechanical formula for pressure in crystal

3.1 Differentiation of the Schrödinger equation for crystal

As mentioned above, a quite quantum mechanical formula for pressure in crystal in terms of *exact* wave functions of the crystal was first derived by N A Dmitriev [34]. The idea of this proof was later used in Ref. [5] for deriving a similar formula based on the HF approximation. The original, quite succinct proof of this formula is, unfortunately, hard to grasp. Because

of this, we (N A Dmitriev and myself) decided to give a more detailed proof of his formula for cold pressure so as to save the reader an extra trip to the library. This job was done by me, and I slightly modified the proof. It is this proof that follows.

The formula for cold pressure is based on the relationship

$$dE_c = -P_c dV \rightarrow P_c = -\frac{dE_c}{dV} = -\frac{d(E_c^{\text{el}} + E_c^{\text{n}})}{dV}, \quad (3.1)$$

which results from the separation $E = E_c + E_{\text{th}}$ in the expression

$$P = -\left(\frac{\partial E}{\partial V}\right)_S \rightarrow P_c = -\left(\frac{\partial E_c}{\partial V}\right)_{S=0},$$

$$P_{\text{th}} = -\left(\frac{\partial E_{\text{th}}}{\partial V}\right)_{S=\text{const} \neq 0}. \quad (3.2)$$

In Eqn (3.1), E_c^{el} is the energy of the ground state of the electron system of crystal, and E_c^{n} is the energy of nuclei (the energy of the crystal lattice). The corresponding parts of the total Hamiltonian are given below in Eqn (3.3). Expression (3.1) was used for deriving the formula for P_c in finite difference form — that is, in the form $P_c = -\Delta E_c/\Delta V$.

So, we are going to express the formula for the mean cold pressure in an isotropic single crystal of volume $\Omega = L^3$, consisting of K cells and N electrons, of normal density ρ . This pressure is caused by isotropic stress applied to the crystal. A cell of crystal may contain several atoms; z_h is the atomic number of the h atom of the cell. Exact translational symmetry can only exist in a perfect crystal of infinite dimensions. Real crystals, however, are finite, and their bounding surfaces break the translational symmetry. If, however, the dimensions L of crystal are large enough compared to the mean length of vectors of the principal translations ($\sim 10^{-7}$ cm), the *bulk* properties of the crystal are practically not affected by the existence of the boundary surfaces. Of course, analytically one has to consider a crystal of infinite size. This requirement amounts to stating such boundary conditions as would ensure complete translational invariance of all physical properties of the crystal. In our case, this means that the exact wave function Ψ of electron system of the crystal must be periodic with respect to the coordinates of each electron — for example,

$$\Psi(x, y, z, s; q_2, q_3, \dots) = \Psi(x + L, y, z, s; q_2, q_3, \dots)$$

$$= \Psi(x, y + L, z, s; q_2, q_3, \dots) = \dots$$

and so on.

The potential energy $U(\mathbf{r})$ of a free electron in a perfect crystal of infinite size is a periodic function with the period of the lattice constant \mathbf{n} : $U(\mathbf{r} + \mathbf{n}) = U(\mathbf{r})$. In other words, when the crystal is translated in space by vector \mathbf{n} , it coincides with itself if the origin of vector \mathbf{n} coincides with one of the lattice points).

The Hamiltonian of the crystal, expressed in the atomic units $\hbar = e = m_e = 1$ and in the zero adiabatic approximation, is

$$H = -\sum_j \frac{\Delta_j}{2} - \sum_{jh} \frac{z_h}{|\mathbf{r}_j - \mathbf{R}_h|} + \frac{1}{2} \sum_{jj'}' \frac{1}{|\mathbf{r}_j - \mathbf{r}_{j'}|}$$

$$+ \frac{1}{2} \sum_{hh'}' \frac{z_h z_{h'}}{|\mathbf{R}_h - \mathbf{R}_{h'}|}. \quad (3.3)$$

We denote the last term in Eqn (3.3) by H_n . The sum of the first three terms is H_{el} . On the other hand, the first term is H_{kin} , and the others give H_C . In the original paper the stress is assumed to be tension. Then the center of the arbitrary cell of the initial state moves to the position $\mathbf{R}'_g = (1 + \varepsilon)\mathbf{R}_g$ (if it is a monatomic cell, its center coincides with the nucleus of the atom). If the initial volume of the crystal is Ω , and the stretched volume is Ω' , then

$$H(\Omega)\Psi = E\Psi, \quad H'(\Omega') = E'\Psi'. \quad (3.4)$$

Should one approach this problem in a *straightforward* manner, this will only lead to the virial theorem. It is this way that has been used in Ref. [43] for quantum mechanical proof of VT to supplant the existing classical proofs [44, 45]⁵. The term ‘virial theorem’ usually refers [44, 45] to the relation between the pressure, the kinetic and the potential parts of the internal energy, and the volume of the system. The VT expression obtained in Ref. [43] is

$$\begin{aligned} 3VP(V, T) &= 3(\gamma - 1)E_{kin}(V, T) + \sum_n nE_n^{pot}(V, T) \\ &= 3(\gamma - 1)E_{kin} + \frac{\sum_n nE_n^{pot}}{\sum_n n} \sum_n n \\ &\approx 3(\gamma - 1)E_{kin}(V, T) + E_{pot}(V, T) \sum_n n. \end{aligned} \quad (3.4a)$$

If we consider matter as the aggregate of interacting electrons and nuclei (then $\gamma = 5/3$, $U(r) \sim A/r$ and hence $\sum_n n \rightarrow 1$), then Eqn (3.4a) assumes its conventional form [44, 45]:

$$3VP(V, T) = 2E_{kin}(V, T) + E_{pot}(V, T). \quad (3.4b)$$

We see that this way does not lead to the goal. This is why Gandel'man and Dmitriev had to find other approaches to the problem. Since, as already said, I dealt with the extension of Dmitriev's formula to the case of finite temperatures, it will be easier for me to explain his method. This is the main reason why I decided not to present Gandel'man's solution, which certainly is very interesting methodologically.

When the volume is changed from Ω to Ω' in problem (3.4), it is possible to establish a one-to-one correspondence between all points of the volumes Ω and Ω' . In place of Ω and Ω' , Dmitriev considered the volumes Ω and Ω'' , with Ω'' defined in the following way: the centers $\mathbf{R}_g \rightarrow \mathbf{R}'_g$ of cells displaced as a result of a self-similar transform $\mathbf{R}' = (1 + \varepsilon)\mathbf{R}$ of volume Ω into volume Ω' are used for constructing new cells of the same size, whose total volume is denoted by Ω'' . It differs from Ω' geometrically and in magnitude only by the aggregate of the gaps, but $\Omega'' = \Omega$. Then a correspondence is established between the points of volumes Ω'' and Ω : the centers of cells in Ω are related to the centers of cells in Ω'' so that all points of cell ω''_i in Ω'' and all points of cell ω_i in Ω are arranged in the same way with respect to their centers. Then,

⁵ The proof of VT for quantum systems based on the transform of scale can be found in the books [6, 46]. The proof of VT in Ref. [43], however, is based on the variation principle of quantum mechanics [47], and is therefore a *direct* approach to the solution of the problem (3.4); secondly, this proof is also good for the case when the potential energy of interaction of structural elements of matter (for example, direct interaction between atoms or molecules) has to be defined as a function of their relative coordinates with a *different* degree of homogeneity: $U(r) \approx \sum_n A_n/r^n \equiv \sum_n U_n(r)$. Unlike that, the proof of VT in Refs [36, 44–46] is given for the potential with a *fixed* degree of homogeneity.

obviously, one and the same point from Ω lying on the *boundary* of the cell ω_i will have *two* corresponding points from Ω'' , located on the opposite sides of the gap separating adjacent cells. Because of this, the wave function Ψ' , continuous in Ω' , will be discontinuous in Ω'' . The scale remains the same because of the correspondence between the points in Ω'' and the points in Ω . Therefore, the kinetic part in H' does not change: $H'_{kin} = H_{kin}$, by contrast to the situation with the virial theorem. The Coulombian part of H' will remain stretched, but integration is not carried out over the volume of the gaps. Given these features of volume $\Omega'' \equiv \Omega$, problem (3.4 can be restated in the form

$$H(\Omega)\Psi^* = E\Psi^*; \quad H'(\Omega) = E'\Psi'. \quad (3.5)$$

Problem (3.5) is a quite equivalent reformulation of the initial problem (3.4). This reformulation can also be conceived in a more natural way: in the course of extension $\mathbf{R}' = (1 + \varepsilon)\mathbf{R}$ one may assume that the nuclei (nucleus) of each cell are fixed to its center, and only the cells are displaced, each as a whole. As already indicated in Section 2.4, the state of the crystal obtained in a such way may turn out to be nonequilibrium in the new volume, but its energy will differ from the energy of the equilibrium state in this volume by an infinitesimal of the second order (since the states themselves differ by an infinitesimal of the first order).

So, we solve problem (3.5): multiply the first equation by Ψ' , the second by Ψ^* , subtract the first from the second, integrate the difference with respect to all $dx_1 \dots dx_N \equiv dQ$ (and with respect to each $x_j \equiv \mathbf{r}_j\sigma_j$ over the entire volume W , where W is Ω plus the volume of spin space; σ_j is the spin coordinate of the j th electron; $dx_j \equiv d\mathbf{r}_j d\sigma_j$):

$$\begin{aligned} &\int_W \dots \int_W (\Psi^* H' \Psi' - \Psi' H \Psi^*) dQ \\ &= (E' - E) \int_W \dots \int_W \Psi^* \Psi' dQ, \end{aligned} \quad (3.6)$$

$$\begin{aligned} H' &= - \sum_j \frac{\Delta_j}{2} + \left(- \sum_{jh} \frac{z_h}{|\mathbf{r}_j - \mathbf{R}_h|'} + \frac{1}{2} \sum_{jj'} \frac{1}{|\mathbf{r}_j - \mathbf{r}_{j'}|'} \right. \\ &\quad \left. + \frac{1}{2} \sum_{hh'} \frac{z_h z_{h'}}{|\mathbf{R}_h - \mathbf{R}_{h'}|'} \right) \equiv H_{kin} + H'_C, \end{aligned} \quad (3.7)$$

where H_{kin} includes the first term, and H'_C the remaining terms. In future we shall need an estimate for $|\mathbf{A} - \mathbf{B}|'$, where point the $A \in \omega_g$ and the point $B \in \omega_{g'}$ are defined by vectors \mathbf{A} and \mathbf{B} with regard to the origin 0, or by vectors \mathbf{A}_g and $\mathbf{B}_{g'}$ with regard to the centers of their respective cells, while the centers are defined by vectors \mathbf{R}_g and $\mathbf{R}_{g'}$ with respect to the origin 0. This quantity can be transformed as follows:

$$\begin{aligned} |\mathbf{A} - \mathbf{B}|' &\equiv |\mathbf{A}' - \mathbf{B}'| = |[(\mathbf{R}_g + \mathbf{A}_g) + \varepsilon\mathbf{R}_g] \\ &\quad - [(\mathbf{R}_{g'} + \mathbf{B}_{g'}) + \varepsilon\mathbf{R}_{g'}]| = |\mathbf{A} - \mathbf{B} + \varepsilon(\mathbf{R}_g - \mathbf{R}_{g'})|. \end{aligned}$$

In the Coulombian part of Eqn (3.6) we can drop the primes at Ψ' : by virtue of the variation principle, the change of the result ($E'_C - E_C$) will then be of the order of ε^2 — in other words, Eqn (3.6) can be rewritten as

$$\begin{aligned} &\int_W \dots \int_W (\Psi^* H_{kin} \Psi' - \Psi' H_{kin} \Psi^*) dQ \\ &\quad + \int_W \dots \int_W (H'_C - H_C) |\Psi|^2 dQ = E' - E. \end{aligned} \quad (3.8)$$

Now we note that the first integral here should have vanished because $H_{\text{kin}}^+ = H_{\text{kin}}$, had Ψ' been continuous in Ω . And one more thing. We can see that the Coulombian part of Eqn (3.8) is real-valued, while the kinetic part is a complex number. Therefore, it is convenient to use Green's formula (see Ref. [48], p. 570)):

$$\begin{aligned} \int_{\Omega} (U_1 \Delta U_2 - U_2 \Delta U_1) dV &= \oint_{\Sigma(\Omega)} (U_1 \nabla U_2 - U_2 \nabla U_1) dS \\ &= \oint_{\Sigma(\Omega)} \left(U_1 \frac{\partial U_2}{\partial n} - U_2 \frac{\partial U_1}{\partial n} \right) dS, \end{aligned} \quad (3.9)$$

where we have used the definition of gradient $\nabla U \equiv \mathbf{n}^0 \partial U / \partial n$, and $\partial U / \partial n$ is taken in the direction of \mathbf{n}^0 . The surface $\Sigma(\Omega)$ in Eqn (3.9) is closed, and therefore the direction of the normal is unambiguous. Then $dS = \mathbf{n}^0 dS$, and $\mathbf{n}^0 \nabla U = \partial U / \partial n$ [and generally $(\mathbf{n}^0 \nabla)^m U \equiv \partial^m U / \partial n^m$] is the derivative over the direction of the outward normal to dS .

3.2 Kinetic part of the total pressure

Returning to Eqn (3.8), it will be convenient also to consider the equations

$$H_{\text{kin}}(\Omega) \Psi = E_{\text{kin}} \Psi, \quad H_{\text{kin}}(\Omega) \Psi'^* = E_{\text{kin}} \Psi'^*$$

for the kinetic part. They will lead to a complex conjugate expression regarding the kinetic part of Eqn (3.8). Their half-sum will give a real quantity: $Z + Z^* = 2 \text{Re } Z$. This remark may be regarded as justification of the procedure by which we add the resulting complex expression for the kinetic part with its complex conjugate and divide by two.

So, we have to consider the kinetic part of the total expression (3.8):

$$\begin{aligned} E'_{\text{kin}} - E_{\text{kin}} &= -\frac{1}{2} \sum_j \int_W \dots \int_W \frac{dQ}{d\mathbf{r}_j} \\ &\times \int_{\Omega} (\Psi^* \Delta_j \Psi' - \Psi' \Delta_j \Psi^*) d\mathbf{r}_j \\ &= \left(-\frac{N}{2} \int_W \dots \int_W \frac{dQ}{d\mathbf{r}} \right) \int_{\Omega} (\Psi^* \Delta_r \Psi' - \Psi' \Delta_r \Psi^*) d\mathbf{r} \\ &\equiv (\dots) \int_{\Omega} (\dots) d\mathbf{r} = (\dots) \sum_g \int_{\omega(g)} (\dots) d\mathbf{r} \\ &= (\dots) \sum_g \oint_{\Sigma(g)} (\Psi^* \nabla_r \Psi' - \Psi' \nabla_r \Psi^*) dS \\ &= (\dots) \sum_g \oint_{\Sigma'(g)} \left(\Psi^* \frac{\partial \Psi'}{\partial n} - \Psi' \frac{\partial \Psi^*}{\partial n} \right) dS. \end{aligned} \quad (3.10)$$

Here the integral with respect to the volume of the cell [and over its surface $\Sigma(g)$] in fact does not depend on the cell number g . Nevertheless, we cannot immediately replace the sum \sum_g with the total number K of cells, since then we would lose the two-sidedness of the cell boundary that appeared for Ψ' in the new volume $\Omega'' \equiv \Omega$. If the volume Ω contains Kn -faced cells ω_g , the sum $(\sum_g \oint dS)$ will contain nK terms, or $K/2$ two-sided n -faced cells. Accordingly, we may write

$$\sum_g \oint_{\Sigma(g)} (\dots) dS = \frac{K}{2} \oint_{\Sigma'(g)} (\dots) dS, \quad (3.11)$$

where $\Sigma'(g)$ implies two-sidedness (for Ψ') of the cell surface, and the surface integral on the right-hand side of Eqn (3.11) is taken over both the outer surface (outward normal) and the inner surface (inward normal). We get

$$\begin{aligned} (3.10) &= -\frac{NK}{4} \int_W \dots \int_W \frac{dQ}{d\mathbf{r}} \oint_{\Sigma'(g)} dS \left(\Psi^* \frac{\partial \Psi'}{\partial n} - \Psi' \frac{\partial \Psi^*}{\partial n} \right) \\ &= -\frac{NK}{4} \int_W \dots \int_W \frac{dQ}{d\mathbf{r}} \oint_{\Sigma(g)} dS \left(\Psi^* \frac{\partial}{\partial n} - \frac{\partial \Psi^*}{\partial n} \right) (\Psi'_+ - \Psi'_-), \end{aligned} \quad (3.12)$$

where the symbols '+' and '-' denote, respectively, the outer and the inner surfaces of the cell. Using the Taylor expansion (see Ref. [49], p. 52)

$$\begin{aligned} f(\mathbf{r} + \varepsilon \mathbf{a}) &= f(\mathbf{r}) + \varepsilon \mathbf{a} \nabla f(\mathbf{r}) + \frac{1}{2!} \varepsilon^2 (\mathbf{a} \nabla)^2 f(\mathbf{r}) \\ &+ \frac{1}{3!} \varepsilon^3 (\mathbf{a} \nabla)^3 f(\mathbf{r}) + \dots \approx f(\mathbf{r}) + \varepsilon (\mathbf{a} \nabla) f(\mathbf{r}) \\ &= f(\mathbf{r}) + \varepsilon \mathbf{a} \mathbf{n}^0 \frac{\partial f}{\partial n} = f(\mathbf{r}) + \varepsilon a_n \frac{\partial f}{\partial n} \end{aligned} \quad (3.13)$$

it is easy to calculate the difference

$$\begin{aligned} \Psi'_+ - \Psi'_- &\equiv \Psi'_+(\mathbf{r}) - \Psi'_-(\mathbf{r} + \varepsilon \mathbf{n} |\mathbf{R}_g - \mathbf{R}_{g'}|) \\ &\approx -\varepsilon |\mathbf{R}_g - \mathbf{R}_{g'}| \frac{\partial \Psi'}{\partial n}, \end{aligned}$$

and the two-sided integration reduces to integration over one (outer) surface:

$$\begin{aligned} (3.10) &= -\varepsilon \frac{NK}{4} \int_W \dots \int_W \frac{dQ}{d\mathbf{r}} \oint_{\Sigma(g)} |\mathbf{R}_g - \mathbf{R}_{g'}| \\ &\times \left(\frac{\partial \Psi^*}{\partial n} \frac{\partial \Psi'}{\partial n} - \Psi^* \frac{\partial^2 \Psi'}{\partial n^2} \right) dS. \end{aligned} \quad (3.14)$$

Here $|\mathbf{R}_g - \mathbf{R}_{g'}|$ is the distance between the centers of the cell ω_g and the adjacent cell $\omega_{g'}$ (which have a common integration surface); in general, this distance may be different for different faces of the cell; $\partial / \partial n \equiv \partial / \partial r_n$ is the derivative with respect to \mathbf{r} in the direction of the outward normal to the face at point \mathbf{r} . Now we may drop the primes in Eqn (3.14), which already is of the order of $\sim \varepsilon$, and carry out integration with respect to all other variables $dQ/d\mathbf{r}$ over the entire volume W . We get

$$\begin{aligned} (3.14) &= -\varepsilon \frac{K}{4} \oint_{\Sigma(g)} |\mathbf{R}_g - \mathbf{R}_{g'}| \\ &\times \left(\frac{\partial^2}{\partial n \partial n'} - \frac{\partial^2}{\partial n^2} \right) \gamma(\mathbf{r}' | \mathbf{r}) \Big|_{\mathbf{r}'=\mathbf{r}} dS, \end{aligned} \quad (3.15)$$

$$\begin{aligned} \gamma(\mathbf{r}' | \mathbf{r}) &\equiv N \int_W \dots \int_W \left[\Psi^*(x_N \dots x_2, \mathbf{r}' \sigma') \Psi(\mathbf{r} \sigma, x_2 \dots x_N) \right. \\ &\times \left. \prod_{j=2}^N dx_j \right]_{\sigma'=\sigma} d\sigma \end{aligned} \quad (3.16)$$

is the electron spinless density matrix of the first order, corresponding to the ground state of the electron system of crystal, $\gamma(\mathbf{r} | \mathbf{r}) \equiv \gamma(\mathbf{r})$ is the density of electrons of the first order; $\gamma^*(\mathbf{r} | \mathbf{r}') = \gamma(\mathbf{r}' | \mathbf{r})$. Adding Eqn (3.15) and its complex conjugate, dividing by two and normalizing to the product of the number of cells K by $|\Delta\omega| = 3|\omega|\varepsilon$ (the change of the

volume $\Delta\Omega = \Omega' - \Omega$ per cell resulting from extension of the crystal), we find the kinetic part of the pressure acting on the arbitrary cell ω_g associated with the change of its equilibrium volume:

$$P_{\text{kin}} \equiv -\frac{\Delta E_{\text{kin}}}{|\Delta\omega|} = \frac{1}{12|\omega|} \oint_{\Sigma(g)} dS |\mathbf{R}_g - \mathbf{R}_{g'}| \times \left(\frac{\partial^2}{\partial n \partial n'} - \frac{\partial^2}{2\partial n^2} - \frac{\partial^2}{2\partial n'^2} \right) \gamma(\mathbf{r}'|\mathbf{r}) \Big|_{\mathbf{r}'=\mathbf{r}}, \quad (3.17)$$

where ω is the cell itself (shape), and $|\omega|$ is its volume.

Since $\oint_{\Sigma(g)} |\mathbf{R}_g - \mathbf{R}_{g'}| dS = 6|\omega_g|$, the kinetic pressure may be regarded as averaging with the weight $|\mathbf{R}_g - \mathbf{R}_{g'}|$ over the surface $\Sigma(g)$ of the cell ω_g of a real quantity

$$P_{\text{kin}}(\mathbf{r}) \equiv \frac{1}{2} \left(\frac{\partial^2}{\partial n \partial n'} - \frac{\partial^2}{2\partial n^2} - \frac{\partial^2}{2\partial n'^2} \right) \gamma(\mathbf{r}'|\mathbf{r}) \Big|_{\mathbf{r}'=\mathbf{r}}. \quad (3.18)$$

Accordingly, Eqn (3.17) may be rewritten as

$$P_{\text{kin}} = \frac{1}{6|\omega|} \oint_{\Sigma(g)} dS |\mathbf{R}_g - \mathbf{R}_{g'}| P_{\text{kin}}(\mathbf{r}). \quad (3.19)$$

A methodological example of the application of Eqn (3.19) is given in Section 8.

3.3 Coulombian part of the total pressure

The analysis of the Coulombian difference in Eqn (3.8) may start with the part corresponding to the interaction of electrons with one another — that is, with the second operator in H_C from Eqn (3.3):

$$\Delta E_C^{(2)} \equiv \frac{1}{2} \sum_{jj'} \int \dots \int \left(\frac{1}{|\mathbf{r}_j - \mathbf{r}_{j'}|} - \frac{1}{|\mathbf{r}_j - \mathbf{r}_{j'}'|} \right) |\Psi|^2 dQ. \quad (3.20)$$

Here the integral in the summand obviously does not depend on j, j' , and so summation can be replaced with multiplication by $N(N-1)$, which gives

$$\Delta E_C^{(2)} = \frac{1}{2} \int_{\Omega} \int_{\Omega} 2 \left[\frac{N(N-1)}{2} \int_W \dots \int_W |\Psi|^2 \frac{dQ}{d\mathbf{r} d\mathbf{r}'} \right] \times (\dots) d\mathbf{r} d\mathbf{r}' = \frac{1}{2} \int_{\Omega} \int_{\Omega} 2\Gamma(\mathbf{r}\mathbf{r}') (\dots) d\mathbf{r} d\mathbf{r}', \quad (3.21)$$

$$\Gamma(\mathbf{r}_2\mathbf{r}_1|\mathbf{r}_1\mathbf{r}_2) \equiv \frac{N(N-1)}{2} \int_W \dots \int_W \left[\Psi^*(x_N \dots x_3 \mathbf{r}'_2 \mathbf{r}'_1 \boldsymbol{\sigma}'_1) \times \Psi(\mathbf{r}_1 \boldsymbol{\sigma}_1 \mathbf{r}_2 \boldsymbol{\sigma}_2 x_3 \dots x_N) \prod_{j=3}^N dx_j \right]_{\boldsymbol{\sigma}'_2=\boldsymbol{\sigma}_2; \boldsymbol{\sigma}'_1=\boldsymbol{\sigma}_1} d\boldsymbol{\sigma}_1 d\boldsymbol{\sigma}_2 \quad (3.22)$$

is the electron spinless density matrix of the *second* order, corresponding to the ground state of the crystal, $\Gamma(\mathbf{r}_2\mathbf{r}_1|\mathbf{r}_1\mathbf{r}_2) \equiv \Gamma(\mathbf{r}_1\mathbf{r}_2)$ is the density of electrons of the second order. Since the crystal under consideration is uniform with respect to its physical properties (all cells have similar shape, and have on the average the same physical properties), the integral $\int_W d\mathbf{r}_2 \int_{\omega(g)} d\mathbf{r}_1 \Gamma(\mathbf{r}_1\mathbf{r}_2) (\dots)$ does not depend on the number g of the selected cell. This allows us to make the following transformations:

$$\int_{\Omega} d\mathbf{r}_2 \int_{\Omega} d\mathbf{r}_1 f = \int_{\Omega} d\mathbf{r}_2 \sum_g \int_{\omega(g)} d\mathbf{r}_1 f \\ = K \int_{\Omega} d\mathbf{r}_2 \int_{\omega(g)} d\mathbf{r}_1 f = K \sum_{g'} \int_{\omega(g')} d\mathbf{r}_2 \int_{\omega(g')} d\mathbf{r}_1 f,$$

where K is the total number of cells in a crystal of volume Ω . The quantity $f \equiv (\dots)$ [see Eqns (3.20) and (3.21)] is easy to calculate using the definition

$$|\mathbf{A} + \varepsilon\mathbf{B}| \equiv [(\mathbf{A} + \varepsilon\mathbf{B})^2]^{1/2} \approx (\mathbf{A}^2 + 2\varepsilon\mathbf{A}\mathbf{B})^{1/2} \\ = A \left(1 + \frac{2\varepsilon\mathbf{A}\mathbf{B}}{A^2} \right)^{1/2} \approx A + \frac{\varepsilon\mathbf{A}\mathbf{B}}{A}.$$

Therefore, the parenthesis (\dots) (which only is nonzero when $g' \neq g$) is

$$(\dots) = \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2 + \varepsilon(\mathbf{R}_g - \mathbf{R}_{g'})|} - \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \\ \approx -\frac{\varepsilon(\mathbf{r}_1 - \mathbf{r}_2)(\mathbf{R}_g - \mathbf{R}_{g'})}{|\mathbf{r}_1 - \mathbf{r}_2|^3},$$

and the integral (3.21) is

$$\Delta E_C^{(2)} = -\frac{K}{2} \sum_{g'}' \varepsilon(\mathbf{R}_g - \mathbf{R}_{g'}) \int_{\omega(g')} d\mathbf{r}_2 \\ \times \int_{\omega(g)} d\mathbf{r}_1 \frac{2\Gamma(\mathbf{r}_1\mathbf{r}_2)(\mathbf{r}_1 - \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|^3} \\ \equiv -\frac{K}{2} \sum_{g'}' \varepsilon(\mathbf{R}_g - \mathbf{R}_{g'}) \mathbf{F}_{gg'}^{ee}. \quad (3.23)$$

We see that this expression describes the work of the force $\mathbf{F}_{gg'}^{ee}$, which is the electron part of the Coulombian interaction of cells $\omega_{g'}$ and ω_g , as the point of its application travels the distance of $(\mathbf{R}_g - \mathbf{R}_{g'})\varepsilon$. This result is equivalent to the statement that the work of force of interaction of two charges (bodies) is the product of this force times the change of the vector connecting their electrical centers (centers of mass). The relevant part of the pressure is obtained by dividing this work by the change in the volume $|\Delta\omega| = 3\varepsilon|\omega|$, since the formula $dA = P(V) dV$ holds in any case. In a similar way, we calculate the work of the force of interaction between the electrons of cell ω_g and nuclei of cell $\omega_{g'}$, nuclei of cell ω_g and electrons of cell $\omega_{g'}$, nuclei of cell ω_g and nuclei of cell $\omega_{g'}$ over the distance $(\mathbf{R}_g - \mathbf{R}_{g'})\varepsilon$ traveled by the point of application of the force, using the differences

$$\frac{1}{|\mathbf{r}_1 - \mathbf{R}_h|'} - \frac{1}{|\mathbf{r}_1 - \mathbf{R}_h|} \approx -\frac{\varepsilon(\mathbf{r}_1 - \mathbf{R}_h)(\mathbf{R}_g - \mathbf{R}_{g'})}{|\mathbf{r}_1 - \mathbf{R}_h|^3}, \quad (\text{A})$$

$$\frac{1}{|\mathbf{R}_h - \mathbf{r}_2|'} - \frac{1}{|\mathbf{R}_h - \mathbf{r}_2|} \approx -\frac{\varepsilon(\mathbf{R}_h - \mathbf{r}_2)(\mathbf{R}_g - \mathbf{R}_{g'})}{|\mathbf{R}_h - \mathbf{r}_2|^3}, \quad (\text{B})$$

$$\frac{1}{|\mathbf{R}_h - \mathbf{R}_h'|'} - \frac{1}{|\mathbf{R}_h - \mathbf{R}_h'|} \approx -\frac{\varepsilon(\mathbf{R}_h - \mathbf{R}_h')(\mathbf{R}_g - \mathbf{R}_{g'})}{|\mathbf{R}_h - \mathbf{R}_h'|^3}. \quad (\text{C})$$

The change of distance between the centers of cells in question is

$$|\mathbf{R}_g - \mathbf{R}_{g'}|' - |\mathbf{R}_g - \mathbf{R}_{g'}| \approx \varepsilon|\mathbf{R}_g - \mathbf{R}_{g'}|.$$

Now it is easy to find [see expression (A)] that

$$\begin{aligned} \Delta E_C^{(1)} &= - \sum_{jh} z_h \int_W \dots \int_W |\Psi|^2 \left(\frac{1}{|\mathbf{r}_j - \mathbf{R}_h|'} - \frac{1}{|\mathbf{r}_j - \mathbf{R}_h|} \right) dQ \\ &= - \sum_h z_h K \int_{\omega(g)} d\mathbf{r} \gamma(\mathbf{r}) (\dots) \\ &= \varepsilon K \int_{\omega(g)} d\mathbf{r} \gamma(\mathbf{r}) \sum_{g'} \sum_{h \in \omega(g')} z_h \int_{\omega(g')} d\mathbf{r}' \\ &\quad \times \frac{(\mathbf{r} - \mathbf{r}')(\mathbf{R}_g - \mathbf{R}_{g'}) \delta(\mathbf{r}' - \mathbf{R}_h)}{|\mathbf{r} - \mathbf{r}'|^3}. \end{aligned} \quad (3.24)$$

Differently from Eqn (3.23), the cells ω_g and $\omega_{g'}$ here are not equivalent: the electrons of cell ω_g interact with the nuclei of cell $\omega_{g'}$ [see expression (A)]. This part can be symmetrized if we take half of its sum with the term describing the interaction of the electrons of cell ω_g with the nuclei of cell $\omega_{g'}$ [see expression (B)]:

$$\begin{aligned} \Delta E_C^{(1)} &= \frac{K}{2} \sum_{g'} (\mathbf{R} - \mathbf{R}_{g'}) \varepsilon \int_{\omega(g')} d\mathbf{r}' \int_{\omega(g)} d\mathbf{r} \frac{\mathbf{r} - \mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|^3} \\ &\quad \times \left[\gamma(\mathbf{r}) \sum_{h' \in \omega(g')} z_{h'} \delta(\mathbf{r}' - \mathbf{R}_{h'}) \right. \\ &\quad \left. + \gamma(\mathbf{r}') \sum_{h \in \omega(g)} z_h \delta(\mathbf{r} - \mathbf{R}_h) \right] \\ &\equiv \frac{K}{2} \sum_{g'} (\mathbf{R}_g - \mathbf{R}_{g'}) \varepsilon (\mathbf{F}_{gg'}^{en} + \mathbf{F}_{gg'}^{ne}). \end{aligned} \quad (3.25)$$

Finally, for the interaction between the nuclei we have [see expression (C)]:

$$\begin{aligned} \Delta E_C^{(3)} &= \frac{1}{2} \sum'_{hh'} z_h z_{h'} \left(\frac{1}{|\mathbf{R}_h - \mathbf{R}_{h'}|'} - \frac{1}{|\mathbf{R}_h - \mathbf{R}_{h'}|} \right) \\ &\quad \times \int_W \dots \int_W |\Psi|^2 dQ = \frac{1}{2} \sum'_{hh'} z_h z_{h'} (\dots) \cdot 1 \\ &= \frac{K}{2} \sum_{g'} \sum_{h \in \omega(g)} z_h \sum_{h' \in \omega(g')} z_{h'} (\dots) \\ &= \left[- \frac{K}{2} \sum_{g'} (\mathbf{R}_g - \mathbf{R}_{g'}) \varepsilon \sum_{h \in \omega(g)} z_h \sum_{h' \in \omega(g')} z_{h'} \right] \frac{\mathbf{R}_h - \mathbf{R}_{h'}}{|\mathbf{R}_h - \mathbf{R}_{h'}|^3} \\ &= [\dots] \int_{\omega(g)} d\mathbf{r} \int_{\omega(g')} d\mathbf{r}' \frac{(\mathbf{r} - \mathbf{r}') \delta(\mathbf{r} - \mathbf{R}_h) \delta(\mathbf{r}' - \mathbf{R}_{h'})}{|\mathbf{R}_h - \mathbf{R}_{h'}|^3} \\ &= - \frac{K}{2} \sum_{g'} (\mathbf{R}_g - \mathbf{R}_{g'}) \varepsilon \mathbf{F}_{gg'}^{nm}. \end{aligned} \quad (3.26)$$

To find the total Coulombian pressure experienced by cell ω_g inside the crystal from the side of all other cells, we must take the sum of expressions (3.23), (3.24) and (3.26), and normalize it to one cell and to the change of its volume $|\Delta\omega_g| = 3\varepsilon|\omega_g| \equiv 3\varepsilon|\omega|$. This gives

$$\begin{aligned} P_C &= \frac{1}{3|\omega|} \sum_{g'} (\mathbf{R}_g - \mathbf{R}_{g'}) \left[\frac{1}{2} \mathbf{F}_{gg'}^{ee} - \frac{1}{2} (\mathbf{F}_{gg'}^{en} + \mathbf{F}_{gg'}^{ne}) \right. \\ &\quad \left. + \frac{1}{2} \mathbf{F}_{gg'}^{nm} \right] \equiv \frac{1}{6|\omega|} \sum_{g'} (\mathbf{R}_g - \mathbf{R}_{g'}) \mathbf{F}_{gg'}, \end{aligned} \quad (3.27)$$

$$\mathbf{F}_{gg'} \equiv \int_{\omega(g')} d\mathbf{r}' \int_{\omega(g)} d\mathbf{r} \frac{\rho(\mathbf{r}, \mathbf{r}') (\mathbf{r} - \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|^3}, \quad (3.28)$$

$$\begin{aligned} \rho(\mathbf{r}, \mathbf{r}') &\equiv 2\Gamma(\mathbf{r}, \mathbf{r}') - \gamma(\mathbf{r}) \sum_{h \in \omega(g')} z_h \delta(\mathbf{r}' - \mathbf{R}_h) \\ &\quad - \gamma(\mathbf{r}') \sum_{h \in \omega(g)} z_h \delta(\mathbf{r} - \mathbf{R}_h) \\ &\quad + \sum_{h \in \omega(g)} z_h \delta(\mathbf{r} - \mathbf{R}_h) \sum_{h' \in \omega(g')} z_{h'} \delta(\mathbf{r}' - \mathbf{R}_{h'}). \end{aligned}$$

This function can be rewritten in a more comprehensible form:

$$\begin{aligned} \rho(\mathbf{r}, \mathbf{r}') &= [2\Gamma(\mathbf{r}, \mathbf{r}') - \gamma(\mathbf{r})\gamma(\mathbf{r}')] + \rho(\mathbf{r})\rho(\mathbf{r}'), \\ \rho(\mathbf{r}) &\equiv \gamma(\mathbf{r}) - \sum_h z_h \delta(\mathbf{r} - \mathbf{R}_h). \end{aligned} \quad (3.29)$$

Then the first equation in (3.29) is the quantum correlation function, and the second, in accordance with Eqn (3.28), gives the purely classical part of the interaction between cells ω_g and $\omega_{g'}$.

4. Quantum statistical formula for the pressure in a crystal

4.1 Several formulas for the pressure at finite temperatures

As a matter of fact, the formula for cold pressure in a crystal allows calculation of the pressure for the case of finite temperature in a similar way. It turns out [39] that this simply requires substituting the temperature matrices $\gamma_\beta(1'1)$, $\Gamma_\beta(2'1'12)$ in place of the cold matrices $\gamma_0(1'1)$, $\Gamma_0(2'1'12)$.

In Ref. [34] the treatment starts with Eqn (3.1), which follows from the basic thermodynamic identity $dE(V, S) = TdS - PdV$ at $T = S = 0$. It is convenient to calculate the pressure in matter in terms of the free energy F :

$$\begin{aligned} P(V, T) &= - \left(\frac{\partial F}{\partial V} \right)_T \rightarrow P_c(V) = - \left(\frac{\partial F_c}{\partial V} \right)_{T=0}, \\ P_{th}(V, T) &= - \left(\frac{\partial F_{th}}{\partial V} \right)_{T \neq 0}, \end{aligned} \quad (4.1)$$

The thermodynamic definition of F is

$$\begin{aligned} F &= E - TS \rightarrow F_c = E_c, \quad F_{th} = E_{th} - TS, \\ dF(V, T) &= -SdT - PdV. \end{aligned} \quad (4.2)$$

Here the differentials dE and dF are expressed in proper variables.

In the book [49], p. 117, one finds another formula for the pressure:

$$P(V, T) = - \frac{\partial}{\partial V} \left[E(V, T) - T \int_0^T \frac{dt}{t} \frac{\partial}{\partial t} E(V, t) \right]. \quad (4.3)$$

It appears, however, that this expression is not quite correct. If the energy has no explicit dependence on the volume, then

the pressure by this formula is zero, which is wrong [50]: in fact, it equals $P(V, T) = T\varphi(V)$. This result is easily obtained by integrating the differential thermodynamic identity

$$T\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial E}{\partial V}\right)_T + P$$

under the condition $(\partial E/\partial V)_T = 0$. The wrong result (4.3) comes from the incorrect solution of equation (25.4) from the same Ref. [49]. Integration of this equation involved division by T without assuming that $T \neq 0$, because of this, one ought to add a singular term of the form $\varphi(V)\delta(T)$ [51, 52], and the correct expression for the pressure would become

$$P(V, T) = -\frac{\partial}{\partial V} \left[E(V, T) - T \int_0^T \frac{dt}{t} \frac{\partial}{\partial t} E(V, t) \right] + \frac{1}{2} T \frac{\partial \varphi}{\partial V}. \quad (4.4)$$

A detailed analysis carried out in Ref. [50] reveals that Eqn (4.3) holds when the entropy of the body tends to zero as $T \rightarrow 0$. If, however, the entropy remains *finite* when $T \rightarrow 0$ — and this is what happens when the internal energy does not depend *explicitly* on the volume — then Eqn (4.4) should be used.

So, the pressure at finite temperatures can be calculated with as many as three thermodynamic expressions given above, along isentropes or isotherms. These formulas reduce to Eqn (3.1) when the temperature tends to zero. Presently we are going to get yet another (this time statistical) formula for the pressure at finite temperatures [see Eqn (4.6)]. This formula also reduces to Eqn (3.1) when the temperature tends to zero.

4.2 Extension of Dmitriev's formula to finite temperatures

The formula for cold pressure is obtained by analytical differentiation of the Schrödinger equation for the ground state Ψ_0 of the electron system of a crystal with respect to its volume (the nuclei of the lattice are regarded to be strictly fixed — that is, zero oscillations of the lattice are not taken into account). The actual differentiation was based on the method of virtual work of small but finite magnitude. However, the examination of the state Ψ_0 , as is shown by the analysis of Ref. [34], was done under the only assumption of the motionless of the lattice nuclei. Given that the following formula must hold for any steady state of the crystal,

$$-\frac{\partial}{\partial V}(E_n^{\text{el}} + E_n^n) = P_n(V), \quad (4.5)$$

which is quite similar to Eqn (4.1), we may immediately conclude that the formula of Ref. [34] for cold pressure should apply to any other steady state Ψ_n of electrons of the crystal, if we replace the matrices γ_0 and Γ_0 of the state Ψ_0 with the matrices γ_n and Γ_n of the state Ψ_n . In other words, the pressure in the crystal can be calculated for *any* steady state Ψ_n using the same Dmitriev formula $P_n = P(\gamma_n, \Gamma_n)$. After that, the expression for P_n must be averaged over the canonical Gibbs ensemble. Then the pressure becomes a function of temperature as well. Equation (4.5) and the statements that follow are derived directly from the defini-

tion of pressure in statistical physics [45]:

$$P(V, T) \equiv -\sum_m W_m \frac{\partial E_m(V)}{\partial V} = \sum_m W_m P_m(V), \quad (4.6)$$

$$W_m \equiv Q^{-1} \exp(-\beta E_m) = \exp \beta (F - E_m),$$

$$H(V)|m\rangle = E_m(V)|m\rangle.$$

The summation in Eqn (4.6) is carried out over the index of state $|m\rangle$ rather than level E_m . Formula (4.6) follows from the statistical definition of free energy

$$\beta F(V, T) \equiv -\ln Q \rightarrow \exp(\beta F) = \frac{1}{Q} \quad (4.7)$$

and the thermodynamic definitions of pressure (4.1) in terms of free energy:

$$\begin{aligned} P &= -\left(\frac{\partial F}{\partial V}\right)_T = -Q^{-1} \sum_n \exp(-\beta E_n) \frac{\partial E_n}{\partial V} \\ &= -\sum_n \exp[\beta(F - E_n)] \frac{\partial E_n}{\partial V}. \end{aligned} \quad (4.8)$$

Hence directly follows the applicability of Eqn (4.6).

4.3 Temperature density matrices

Since the quantities $P_n(V)$, according to Ref. [34], are *linear* functions of the matrices γ_n and Γ_n of state Ψ_n , the pressure P_β by formula (4.6) will be expressed from the temperature matrices in the same way as $P_x(V)$ is expressed from the cold matrices γ_0 and Γ_0 , if the temperature matrices are defined as follows [39]:

$$\begin{aligned} \gamma_\beta(1'|1) &\equiv \sum_n \exp[\beta(F - E_n)] \gamma_n(1'|1) \\ &= N \sum_n \exp[\beta(F - E_n)] \int_W \dots \int_W \Psi^*(x_N \dots x_2 x_1') \\ &\quad \times \Psi(x_1 \dots x_N) dx_2 \dots dx_N, \end{aligned} \quad (4.9)$$

$$\begin{aligned} \Gamma_\beta(2'1'|12) &\equiv \sum_n \exp[\beta(F - E_n)] \Gamma_n(2'1'|12) \\ &= \frac{N(N-1)}{2} \sum_n \exp[\beta(F - E_n)] \\ &\quad \times \int_W \dots \int_W \Psi^*(x_N \dots x_3 x_2' x_1') \Psi(x_1 \dots x_N) dx_3 \dots dx_N. \end{aligned} \quad (4.10)$$

Here we assume that the exact wave functions are normalized in W to unity. Therefore, their traces give, respectively, the number of electrons and the number of different pairs of them in the systems. These matrices at $\beta \rightarrow \infty$ become γ_0 and Γ_0 , respectively, if the state Ψ_0 corresponds to a nondegenerate level E_0 .

So, for calculating the pressure in crystal at finite temperature, one only has to make the replacement $\gamma_0 \rightarrow \gamma_\beta$, $\Gamma_0 \rightarrow \Gamma_\beta$ in formulas (4) and (7) of Ref. [34] [or Eqn (3.17) and (3.28) of this review].

We end this section with the following remark. Matrices (4.9), (4.10) — that is, one and two-electron temperature matrices — can also be obtained from the statistical density

matrix (see Ref. [46], p. 80)

$$\begin{aligned} \rho(x'|x) &\equiv Q^{-1}(V, T, N) \sum_n \exp(-\beta E_n) \Psi_n^*(x') \Psi_n(x) \\ &= \sum_n \exp[\beta(F - E_n)] \Psi_n^*(x') \Psi_n(x), \end{aligned}$$

which corresponds to the canonical Gibbs distribution, if we carry out integration with respect to all variables ($x \equiv x_1 \dots x_N$) but one (for example, x_1) or two (for example, x_1 and x_2) respectively:

$$\gamma_\beta(1'|1) = N \int_W \dots \int_W \rho(x_N \dots x_2 x_1' | x_1 \dots x_N) dx_2 \dots dx_N, \quad (4.11)$$

$$\begin{aligned} \Gamma_\beta(2'1'|12) &= \frac{N(N-1)}{2} \\ &\times \int_W \dots \int_W \rho(x_N \dots x_3 x_2' x_1' | x_1 \dots x_N) dx_3 \dots dx_N. \end{aligned} \quad (4.12)$$

In quantum mechanics, the analogue of the statistical density matrix is the quantum mechanical density matrix $\Psi^*(x')\Psi(x)$, where $\Psi(x)$ is the exact wave function of a certain state of system of N particles (usually the ground state).

5. Method of partial diagonalization of the Hamiltonian of a system with a two-particle interaction

5.1 Hartree – Fock equations: partial diagonalization of the Hamiltonian

Now we are going to use the HF approximation — the main one-particle approximation for a system of many interacting particles — as a model for illustrating the simple analytical method of partial (incomplete) diagonalization of Hamiltonian. In addition to its analytical simplicity, this method has two other advantages over the conventional variation technique: firstly, it directly points to the simplest way to extend the cold HF approximation to the case of finite temperatures, and secondly, prompts a simple technique for finding the exact form of the cold and temperature first-order density matrices (FODM) in the one-particle approximation.

The Hamiltonian of the dynamic system under consideration is usually made up of two parts, diagonal and nondiagonal. In such a case, any approximation used for describing this system may be represented in the language of its Hamiltonian as a partial diagonalization of its nondiagonal part. In such an approximation, the remaining off-diagonal part of the Hamiltonian is simply discarded. If the approximation in question gives a reasonably adequate description of the dynamic behavior, one may assume that the discarded part of the initial Hamiltonian is small. Such partial diagonalization is often best accomplished by going over to *new* one-particle states in the initial Hamiltonian (we assume that it is expressed in terms of occupation of one-particle states). The transform most commonly used for this purpose is the canonical $u-v$ Bogolyubov transform [53]. After the calculation of physical properties of particles introduced in this way (for example, the law of dispersion), the transition is made back to the particles occurring in the initial Hamiltonian. Sometimes such partial diagonalization can be carried out directly in the *initial* Hamiltonian. Then the

physical meaning of the approximation is especially clear and conspicuous. This feat is possible for the Hamiltonian with a two-electron interaction in the HF approximation [54].

Consider the Hamiltonian in the conventional two-electron form

$$H = \sum_{12} \langle 2|h|1 \rangle \hat{b}_2^+ \hat{b}_1 + \frac{1}{2} \sum_{1234} \left\langle 43 \left| \frac{1}{r} \right| 12 \right\rangle \hat{b}_4^+ \hat{b}_3^+ \hat{b}_1 \hat{b}_2, \quad (5.1)$$

where h includes the kinetic energy of particles and the external field (for example, the field of fixed atoms of the lattice). Using the appropriately modified method of schemes [55], it is easy to find the *exact* decomposition (see paragraph 2 of the Appendix)

$$\begin{aligned} H &= \sum_{23} \langle 3|h|2 \rangle \hat{b}_3^+ \hat{b}_2 + \frac{1}{2} \sum_{12} \hat{n}_2 \hat{n}_1 (\langle 21|12 \rangle - \langle 12|12 \rangle) \\ &+ \sum_{123} (\langle 31|12 \rangle - \langle 31|21 \rangle) \hat{b}_3^+ \hat{b}_2 \hat{n}_1 \\ &+ \frac{1}{2} \sum'_{1234} \langle 43|12 \rangle \hat{b}_4^+ \hat{b}_3^+ \hat{b}_1 \hat{b}_2, \quad \hat{n}_i \equiv \hat{b}_i^+ \hat{b}_i. \end{aligned} \quad (5.2)$$

Here we have *explicitly* set apart *all* terms from Eqn (5.1) that are diagonal with respect to two indices or one (terms that have three or four equal indices are simply zero), and use the abbreviated notation $\langle lk|1/r|ij \rangle \equiv \langle lk|ij \rangle$. In the third sum we may assume that $1 \neq 2$, $1 \neq 3$, since for $1 = 2$ or $1 = 3$ we get zero in the brackets (for symmetrical two-particle potential we have $\langle lk|ij \rangle = \langle kl|ji \rangle$). The method of partial diagonalization of the Hamiltonian is based on the assumption that its quantum mechanical averaging will be carried out with respect to the state taken as one determinant. Then the last term in Eqn (5.2) can be simply dropped (since it contributes nothing in this case), and in the second and third sums the operators $\hat{n}_2 \hat{n}_1$ and \hat{n}_1 can be replaced with their averages $\langle D|\hat{n}_1 \hat{n}_2|D \rangle = \langle D|\hat{n}_1|D \rangle \langle D|\hat{n}_2|D \rangle \equiv n_1 n_2$ (in the second sum we assume that $2 \neq 1$, since the term with $2 = 1$ is zero), and $\langle D|\hat{n}_1|D \rangle \equiv n$, respectively. If the states $|j \rangle$ in the determinant $|D \rangle$ are occupied without gaps, then $n_j = 1$ for $\varepsilon_j \leq \varepsilon_F$, and $n_j = 0$ for $\varepsilon_j > \varepsilon_F$, where ε_j is the energy of electron in the state $|j \rangle$, and ε_F is the Fermi energy of the unperturbed system. Thus, Eqn (5.2) for the case under consideration can be rewritten as

$$\begin{aligned} H &= \frac{1}{2} \sum_{12} n_2 n_1 (\langle 21|12 \rangle - \langle 21|21 \rangle) + \sum_{23} \langle 3|h|2 \rangle \hat{b}_3^+ \hat{b}_2 \\ &+ \sum_{23} \left[\sum_1 n_1 (\langle 31|12 \rangle - \langle 31|21 \rangle) \right] \hat{b}_3^+ \hat{b}_2 \\ &\equiv E_0 + \sum_{23} \langle 3| \left[\left(h + \sum_1 n_1 \left\langle 1 \left| \frac{1}{r} \right| 1 \right\rangle \right) |2 \right\rangle \right. \\ &\quad \left. - \sum_1 n_1 \left\langle 1 \left| \frac{1}{r} \right| 2 \right\rangle \right] |1 \rangle \hat{b}_3^+ \hat{b}_2. \end{aligned} \quad (5.2a)$$

Now we see that if we also impose the requirement

$$\begin{aligned} \left(h + \sum_1 n_1 \left\langle 1 \left| \frac{1}{r} \right| 1 \right\rangle \right) |2 \rangle - \sum_1 n_1 \left\langle 1 \left| \frac{1}{r} \right| 2 \right\rangle |1 \rangle &= \varepsilon_2 |2 \rangle, \\ n_1 = 0; 1, \end{aligned} \quad (5.3)$$

we achieve the best possible diagonalization of the Hamiltonian in the case when the wave function of the system is

represented by one determinant made up from one-electron functions. The best diagonalized Hamiltonian (5.2a) then takes the form of the one-particle Hamiltonian

$$H = E_0 + \sum_{12} \varepsilon_2 \hat{b}_3^\dagger \hat{b}_2 \delta_{23} = E_0 + \sum_1 \varepsilon_1 \hat{n}_1 \quad (5.4)$$

and therefore a part of the two-particle interaction, namely

$$\frac{1}{2} \left(\sum_{1234} - \sum'_{1234} \right) \langle 43|12 \rangle \hat{b}_4 \hat{b}_3 \hat{b}_1 \hat{b}_2,$$

is jammed into the self-consistent one-particle potential. Equations (5.3) are one-particle nonlinear integro-differential self-consistent equations. They coincide with the known HF equations that are usually derived by minimizing the Hamiltonian (5.1) with respect to functions of the system expressed as one determinant [47] — that is, from the condition of the minimum of the quantity $\langle D|H|D \rangle$. It is assumed that the one-electron functions $|j\rangle$ are orthonormal, which is not an additional requirement in the case of a determinant. If we drop the second sum in Eqn (5.3) (the exchange term), what remains is the Hartree equation.

From quantum mechanical equations (5.3) we immediately see one of the simplest ways to extend the cold HF equation to the case of finite temperatures: for this purpose, the *quantum mechanical* average values must be interpreted as *quantum statistical* means. Then, however, the one-particle self-consistent potential will no longer depend on the sought one-particle state, and self-consistency is lost. This potential is replaced by the potential statistically averaged over all one-particle states of the system, and therefore *common* for all states. Such a treatment is entirely in the spirit of quantum statistics. So, at $T = 0$ Eqn (5.3) involves the quantum mechanical averages with respect to the ground state of the system, which is the one-determinant function of given order and then $n = 0, 1$. At $T \neq 0$ we have the quantum statistical means instead, and then the trace is taken with respect to all determinants of a given order, and with respect to determinants of all orders; then

$$0 \leq n_1 \equiv \frac{1}{\exp[\beta(\varepsilon_1 - \varepsilon_F)] + 1} \leq 1. \quad (5.4a)$$

The ‘hot’ equations like Eqn (5.3) were obtained in a rather complicated manner (but apparently for the first time ever) in Gandel’man’s paper [1], although in our literature we often find references to the book by Kirzhnits [36], where the result is obtained in a somewhat different (but not any simpler) way than in Ref. [1]. Equations like (5.3) are obtained in a very simple manner in the author’s work [54].

5.2 Density matrices in the one-particle approximation

The HF equations (5.3) offer a very simple method for expressing the *exact* form of FODM — that is, the form of the cold matrix

$$\gamma_n(x'|x) \equiv N \int_W \dots \int_W \Psi_n^*(x_N \dots x_2 x') \Psi_n(x x_2 \dots x_N) \prod_{j=2}^N dx_j \quad (5.5)$$

and the temperature FODM (4.9) in the one-particle approximation. Here the FODM (5.5) corresponds to one concrete state of the electron system of the crystal, and its spinless form

for the ground state is given by Eqn (3.16). The general form of the exact second-order density matrix is found from Eqn (3.22) in a similar way — by eliminating the integration with respect to σ_1 and σ_2 , and therefore eliminating the conditions $\sigma'_2 = \sigma_2, \sigma'_1 = \sigma_1$. It also ought to be noted that the arguments of density matrices denote the points in *space* (ordinary and spin space), rather than the space *coordinates* of individual particles of the system, which are the arguments of the wave functions used for construction of the density matrices.

The one-particle equations (5.3) can be written in the form

$$\left[h + \int_W dx' \frac{\gamma(x'|x')}{|\mathbf{r} - \mathbf{r}'|} \right] \varphi_2(x) - \int_W dx' \frac{\gamma(x'|x) \varphi_2(x')}{|\mathbf{r} - \mathbf{r}'|} = \varepsilon_2 \varphi_2(x), \quad (5.6)$$

if the FODM in the one-particle approximation is written as

$$\begin{aligned} \gamma(x'|x) &\equiv \sum_1 n_1 \varphi_1^*(x') \varphi_1(x) \\ &= \sum_t \sum_\alpha n_{t\alpha} \psi_t^*(\mathbf{r}') S_\alpha^*(\sigma') \psi_t(\mathbf{r}) S_\alpha(\sigma), \end{aligned} \quad (5.7)$$

where the summation index ‘1’ is $t\alpha$, the one-electron wave functions ψ_t are normalized to the volume Ω , and the trace of matrix (5.7) is

$$\text{tr } \gamma(x'|x) \equiv \sum_1 n_1 \int_W |\varphi_1(x)|^2 dx = \sum_1 n_1 = \langle N \rangle.$$

If $n_{t\alpha}$ does not depend on α , then Eqn (5.7) becomes

$$\gamma(x'|x) = \sum_t n_t \psi_t^*(\mathbf{r}') \psi_t(\mathbf{r}) \delta_{\sigma\sigma'}, \quad (5.8)$$

because the spin functions of the particle satisfy the conditions of completeness $\sum_\alpha S_\alpha^*(\sigma') S_\alpha(\sigma) = \delta_{\sigma\sigma'}$ and orthogonality $\sum_\sigma S_\alpha^*(\sigma) S_\alpha(\sigma) = \delta_{\alpha\alpha'}$. The index of state α and the representation index σ of the spin function $S_\alpha(\sigma)$ of the particle take on values from one and the same interval $[-s \leq \alpha, \sigma \leq s]$, where s is the spin of particles in units of \hbar , and the function $S_\alpha(\sigma)$ is defined in such a way that it can actually be represented by the Kronecker delta function: $S_\alpha(\sigma) \equiv \delta_{\alpha\sigma}$.

If summation over ‘1’ (or t and α) in Eqn (5.7) is only carried out with respect to occupied states φ_1 , then the matrix (5.7) is the ordinary cold FODM (5.5) taken in the one-particle approximation. If, however, summation with respect to ‘1’ in Eqn (5.7) is performed over all possible values from the interval given by Eqn (5.4a), then Eqn (5.7) is the one-particle approximation for the temperature FODM (4.9). The matrix (5.7) is the most general representation of FODM in the one-particle approximation. In order to find FODM in a particular one-particle approximation (Thomas–Fermi, Hartree, Hartree–Fock, etc.), into Eqn (5.7) one must substitute the one-particle functions found from the relevant equations. Thus, the form of Eqn (5.7) does not depend on the way in which the total function of the entire system of particles is constructed from the one-particle functions: simple product, determinant, etc. The form of the two-particle density matrix in the one-particle approximation, however, will depend on these factors (see below). In the case of finite temperatures, the matrix (5.7) loses the property $\gamma^2 = \gamma$, which holds for any matrix (5.5) taken in the one-

particle approximation,

$$[\gamma(x'|x)]^2 \equiv \int_W \gamma(x'|x'')\gamma(x''|x) dx'' = \gamma(x'|x) \quad (5.9)$$

by virtue of φ_1 being orthonormal. Equation (5.9) is the continuous counterpart of the discrete relation

$$A^2 = A \rightarrow (A^2)_{jj'} \equiv \sum_{j''} A_{jj''} A_{j''j'} = A_{jj'},$$

which in the general case, of course, does not hold. The loss of projectivity in Eqn (5.7) is associated with the inequality $n_j^2 \neq n_j$, although it can be demonstrated that in the HF approximation (with the determinant representation of the total wave function of the system), the matrices $\Gamma_0(2'1'|12)$ and $\Gamma_\beta(2'1'|12)$ are expressed via $\gamma_0(1'|1)$ and $\gamma_\beta(1'|1)$ in the same way:

$$\Gamma^{\text{HF}}(2'1'|12) = \frac{1}{2} [\gamma(1'|1)\gamma(2'|2) - \gamma(2'|1)\gamma(1'|2)]. \quad (5.10)$$

Therefore, the density of electrons of the second order is expressed in terms of the density of electrons of the first order in the following way:

$$2\Gamma^{\text{HF}}(21|12) - \gamma(1|1)\gamma(2|2) = -|\gamma(2|1)|^2. \quad (5.11)$$

In the Hartree approximation (with the total wave function of the system represented by simple product), the matrix (5.10) is

$$\Gamma^{\text{H}}(2'1'|12) = \gamma(1'|1)\gamma(2'|2). \quad (5.12)$$

Finally, we ought to mention that Eqn (5.7) can be derived from definition (4.9) in a different way, by substituting the total wave function of the entire system in the form of a determinant of one-particle functions.

6. Some one-particle mean expressions for the Hamiltonian with a two-particle interaction

For reference purposes, we can write for Hamiltonian (3.3) several *one-electron* mean expressions which are useful in applications.

1. The wave function of the entire electron system of crystal is represented by the simple product $|\Pi\rangle$ of one-electron functions:

$$|\Pi\rangle = \prod_j^N \varphi_j(x_j) \equiv \prod_j \psi_j(\mathbf{r}_j) S_{\alpha(j)}(\boldsymbol{\sigma}_j). \quad (6.1)$$

Then the mean value of Hamiltonian (3.3) is

$$\langle \Pi | H | \Pi \rangle - E_n = -\frac{1}{2} \int_W [\Delta_{\mathbf{r}} \gamma(x'|x)]_{x'=x} dx + \int_W U(\mathbf{r}) \gamma(x) dx + \frac{1}{2} \int_W \int_W \frac{\gamma(x')\gamma(x)[dx' dx]}{|\mathbf{r} - \mathbf{r}'|}. \quad (6.2)$$

Here we use the notation

$$E_n = \frac{1}{2} \sum_{hh'}' \frac{z^2}{|\mathbf{R}_h - \mathbf{R}_{h'}|}, \quad [dx' dx] \equiv dx' dx \text{ for } \mathbf{r}' \neq \mathbf{r}.$$

(a) If $\varphi_j(x)$ in $|\Pi\rangle$ satisfy the Hartree equations

$$\left[-\frac{\Delta_{\mathbf{r}(j)}}{2} + U(\mathbf{r}_j) + \int_W \frac{\gamma(x') [dx']}{|\mathbf{r}_j - \mathbf{r}'|} \right] \varphi_j(x_j) = \varepsilon_j^{\text{H}} \varphi_j(x_j), \quad (6.3)$$

then we can multiply Eqn (6.3) by $\varphi_j^*(x_j)$ and carry out integration over the entire volume W to get

$$\int_W \left[-\frac{\Delta_{\mathbf{r}}}{2} + U(\mathbf{r}) \right] \gamma(x'|x) dx + \int_W \int_W \frac{\gamma(x')\gamma(x) dx' dx}{|\mathbf{r} - \mathbf{r}'|} = \sum_j \varepsilon_j^{\text{H}}. \quad (6.4)$$

Then Eqn (6.2) can be rewritten in the form

$$\langle \Pi | H | \Pi \rangle^{\text{H}} - E_n = \sum_j \varepsilon_j^{\text{H}} - \frac{1}{2} \int_W \int_W \frac{\gamma(x')\gamma(x) dx' dx}{|\mathbf{r} - \mathbf{r}'|}. \quad (6.5)$$

(b) If $\varphi_j(x)$ in $|\Pi\rangle$ satisfy the HF equations (5.3) or (5.6), and therefore the condition [obtained in the same way as Eqn (6.4)]

$$\sum_j \varepsilon_j^{\text{HF}} = \int_W \left[-\frac{\Delta_{\mathbf{r}}}{2} + U(\mathbf{r}) \right] \gamma(x'|x) \Big|_{x'=x} dx + \int_W \int_W \frac{dx' dx}{|\mathbf{r} - \mathbf{r}'|} [\gamma(x')\gamma(x) - |\gamma(x'|x)|^2], \quad (6.6)$$

the expression (6.2) becomes

$$\langle \Pi | H | \Pi \rangle^{\text{HF}} - E_n = \sum_j \varepsilon_j^{\text{HF}} - \frac{1}{2} \int_W \int_W \frac{\gamma(x')\gamma(x)}{|\mathbf{r} - \mathbf{r}'|} dx' dx + \int_W \int_W \frac{|\gamma(x'|x)|^2}{|\mathbf{r} - \mathbf{r}'|} dx' dx. \quad (6.7)$$

2. The wave function of the entire system is represented by the determinant

$$|D\rangle \equiv \det |\varphi_j(x_j)| = \frac{1}{N!} \sum_p (-1)^p \hat{P} \left[\prod_j \varphi_j(x_j) \right]. \quad (6.8)$$

Here \hat{P} is the operator that performs $N!$ permutations of coordinates x_j of the electrons, p is the order of given permutation with respect to the initial arrangement, the factor $1/N!$ ensures that Eqn (6.8) is normalized when the one-electron functions are normalized. Using Eqn (6.8) in place of (6.1) we get

$$\langle D | H | D \rangle - E_n = -\frac{1}{2} \int_W [\Delta_{\mathbf{r}} \gamma(x'|x)]_{x'=x} dx + \int_W U(\mathbf{r}) \gamma(x) dx + \frac{1}{2} \int_W \int_W \frac{dx' dx}{|\mathbf{r} - \mathbf{r}'|} [\gamma(x')\gamma(x) - |\gamma(x'|x)|^2]. \quad (6.9)$$

(a) If $\varphi_j(x)$ in Eqn (6.8) satisfy the Hartree equations, then Eqn (6.9) becomes

$$\langle D|H|D \rangle^H - E_n = \sum_j \varepsilon_j^H - \frac{1}{2} \int_W \int_W \frac{\gamma(x')\gamma(x)}{|\mathbf{r} - \mathbf{r}'|} dx' dx - \frac{1}{2} \int_W \int_W \frac{|\gamma(x')\gamma(x)|^2}{|\mathbf{r} - \mathbf{r}'|} dx' dx. \quad (6.10)$$

(b) If $\varphi_j(x)$ in Eqn (6.8) satisfy the HF equations, then Eqn (6.9) becomes

$$\langle D|H|D \rangle^{\text{HF}} - E_n = \sum_j \varepsilon_j^{\text{HF}} - \frac{1}{2} \int_W \int_W \frac{\gamma(x')\gamma(x)}{|\mathbf{r} - \mathbf{r}'|} dx' dx + \frac{1}{2} \int_W \int_W \frac{|\gamma(x')\gamma(x)|^2}{|\mathbf{r} - \mathbf{r}'|} dx' dx. \quad (6.11)$$

Now we might ask whether it is necessary to consider the cases when the one-electron functions in the total (non-symmetrized) wave function $|II\rangle$ of the system are represented by the Hartree–Fock functions, and the total antisymmetric function $|D\rangle$ of the system involves the Hartree functions — that is, the hybrids of Eqns (6.7) and (6.10). In the first place, there is nothing theoretically inadmissible in such a combination. Such averages will be simply a little higher than those corresponding to the ‘pure’ cases. At the same time, such a scheme greatly simplifies numerical calculations and reduces their laboriousness. Secondly, it is possible to evaluate the error introduced by such an assumption [2]. Assume, for example, that the HF one-electron functions in $|D\rangle$ are replaced with the Hartree functions (only the spatial parts). Then, using the definitions

$$E_{\text{HF}}(\psi_H) \equiv E_H(\psi_H) + E_{\text{ex}}(\psi_H), \\ E_{\text{HF}}(\psi_{\text{HF}}) \equiv E_H(\psi_{\text{HF}}) + E_{\text{ex}}(\psi_{\text{HF}})$$

and noting that ψ_H minimize E_H , and ψ_{HF} minimize E_{HF} , we may write

$$E_H(\psi_H) - E_H(\psi_{\text{HF}}) < 0, \quad E_{\text{HF}}(\psi_H) - E_{\text{HF}}(\psi_{\text{HF}}) > 0.$$

Hence

$$E_{\text{HF}}(\psi_H) - E_{\text{HF}}(\psi_{\text{HF}}) < E_{\text{ex}}(\psi_H) - E_{\text{ex}}(\psi_{\text{HF}}),$$

and the error introduced into the total energy is less than the error introduced into the exchange part. If the HF one-particle functions differ little from the Hartree functions, which often is the case, the error in the exchange part of the energy will be small compared to the exchange energy itself, and the error in the total energy will be even smaller, which at first glance is certainly not obvious.

Nevertheless, one must always keep in mind that the Hartree functions are obtained when the mean value of the Hamiltonian is minimized with respect to the functions $|II\rangle$ of the system, and the HF functions correspond to minimization with respect to the functions $|D\rangle$, and the only allowable wave function for the electron subsystem can only be the total function antisymmetrical with respect to pairs of electron coordinates — that is, a function of type $|D\rangle$. The requirements on the type of commutation symmetry of the total wave function of the system of identical particles, not in the standard scheme of Ref. [56], are discussed in detail in the author’s paper [57].

7. Exact formula for the pressure in the Hartree–Fock model

The formula for the cold pressure is derived for the case when the crystal cell may contain several nuclei of different kinds. For crystals built of nuclei of one and the same kind, equations (3.27), (3.28) become

$$P_C = \frac{1}{6|\omega|} \sum_{\mathbf{R} \neq 0} \int_{\omega} d\mathbf{r}_2 \times \int_{\omega} d\mathbf{r}_1 f(\mathbf{r}_1, \mathbf{R} + \mathbf{r}_2) (\mathbf{R} + \mathbf{r}_2 - \mathbf{r}_1) \frac{\mathbf{R}}{|\mathbf{R} + \mathbf{r}_2 - \mathbf{r}_1|^3} = \frac{1}{6|\omega|} \sum_{\mathbf{R} \neq 0} \int_{\omega} d\mathbf{r}_2 \int_{\omega} d\mathbf{r}_1 f(\mathbf{r}_1, \mathbf{R} + \mathbf{r}_2) \times \left[\frac{d}{d\lambda} \frac{\lambda}{|\mathbf{R} + \lambda(\mathbf{r}_2 - \mathbf{r}_1)|} \right]_{\lambda=1}, \quad (7.1)$$

where \mathbf{R} goes from the center of cell ω and runs through the centers of all other cells, and the density function is [see also Eqn (3.29)]

$$f(\mathbf{r}_1, \mathbf{R} + \mathbf{r}_2) = 2\Gamma(\mathbf{r}_1, \mathbf{R} + \mathbf{r}_2) - z\gamma(\mathbf{r}_1)\delta(\mathbf{r}_2) - z\gamma(\mathbf{R} + \mathbf{r}_2)\delta(\mathbf{r}_1) + z^2\delta(\mathbf{r}_1)\delta(\mathbf{r}_2). \quad (7.2)$$

In this expression $\gamma(x|x) \equiv \gamma(x)$ and $\Gamma(x'|x|x) \equiv \Gamma(x, x')$ are the densities of electrons of the first and second orders; the first term describes the interaction of two electrons occurring at points \mathbf{r}_1 and $\mathbf{R} + \mathbf{r}_2$ (that is, in different cells, because $\mathbf{R} \neq 0$), the second and third terms describe the interaction of electrons of one cell with the nucleus of another cell, the fourth describes the interaction of nuclei of the cells. Function (7.2) can be represented in a more comprehensible way [see Eqn (3.29)]:

$$f(\mathbf{r}_1, \mathbf{R} + \mathbf{r}_2) = 2\Gamma(\mathbf{r}_1, \mathbf{R} + \mathbf{r}_2) - \gamma(\mathbf{r}_1)\gamma(\mathbf{R} + \mathbf{r}_2) + [\gamma(\mathbf{r}_1) - z\delta(\mathbf{r}_1)][\gamma(\mathbf{R} + \mathbf{r}_2) - z\delta(\mathbf{r}_2)].$$

Here the second term appears as a product $\gamma(\mathbf{r}_1)\gamma(\mathbf{r}_2)$ and corresponds to the interaction between neutral (on average) cells. Since the distribution of the electron charge in the cell is almost spherically symmetrical (because of the cubic symmetry of crystals), this term is actually very small, since the contribution actually comes from the higher multipoles.

In the HF approximation, the coordinate-wise one-electron density matrix and the electron densities of the 1st and 2nd order for the crystal are

$$\gamma(\mathbf{r}_2|\mathbf{r}_1) = \sum_j \psi_j^*(\mathbf{r}_2)\psi_j(\mathbf{r}_1) \sum 1_{\alpha(j)} = \gamma^+(\mathbf{r}_2|\mathbf{r}_1) + \gamma^-(\mathbf{r}_2|\mathbf{r}_1),$$

$$\gamma^\pm(\mathbf{r}_2|\mathbf{r}_1) \equiv \sum_j^\pm \psi_j^*(\mathbf{r}_2)\psi_j(\mathbf{r}_1),$$

$$\gamma(\mathbf{r}) \equiv \sum_j |\psi_j|^2 = \gamma^+(\mathbf{r}) + \gamma^-(\mathbf{r}),$$

$$2\Gamma(\mathbf{r}_1, \mathbf{r}_2) - \gamma(\mathbf{r}_1)\gamma(\mathbf{r}_2) = -|\gamma^+(\mathbf{r}_2|\mathbf{r}_1)|^2 - |\gamma^-(\mathbf{r}_2|\mathbf{r}_1)|^2. \quad (7.3)$$

The kinetic pressure (3.17) in the HF approximation is given by

$$P_{\text{kin}} = \frac{1}{6|\omega|K} \int_{\Sigma(\omega)} dS r_n \left(\frac{\partial^2}{\partial n \partial n'} - \frac{\partial^2}{2\partial n^2} - \frac{\partial^2}{2\partial n'^2} \right) \times \gamma(\mathbf{r}'|\mathbf{r}) \Big|_{\mathbf{r}'=\mathbf{r}}. \quad (7.4)$$

Here r_n is the distance from the center of the cell to the face over which the integration is carried out; $\partial/\partial n$ is the derivative with respect to \mathbf{r} in the direction of outward normal to the face at point \mathbf{r} . Formulas (7.3), (7.4) already involve the one-electron functions obtained from the solution of HF equations for the cold crystal. Now we should make a few remarks concerning Eqn (7.4). This formula can also be found in Ref. [5] in the complex form (see Eqn (4) in Ref. [5]). The key milestones in its derivation are the following. In the HF approximation, the adopted scheme (see Eqn (3.10) or Ref. [5]) yields ($\hbar = e = m_e = 1$)

$$P_{\text{kin}} = \frac{1}{6|\omega|K} \lim_{\varepsilon \rightarrow 0} \sum_t \int_{\omega} [\psi_t^*(\mathbf{r}) \Delta \psi_t'(\mathbf{r}) - \psi_t'(\mathbf{r}) \Delta \psi_t^*(\mathbf{r})] d\mathbf{r}, \quad (7.5)$$

where $\psi_t(\mathbf{r})$ satisfies Bloch's condition (2.2) on the boundary of the cell ω , and ψ_t' on the boundary of the cell ω' . Now in Eqn (7.5) we use Green's formula (3.9):

$$P_{\text{kin}} = \frac{1}{6|\omega|K} \lim_{\varepsilon \rightarrow 0} \sum_t \int_{\Sigma(\omega)} dS \left[\psi_t^*(\mathbf{r}) \frac{\partial \psi_t'(\mathbf{r})}{\partial n} - \psi_t'(\mathbf{r}) \frac{\partial \psi_t^*(\mathbf{r})}{\partial n} \right]. \quad (7.6)$$

Here the total integral over the faces of the surface $\Sigma(\omega)$ of the cell ω is nonzero only because ψ_t' on these faces does not satisfy Bloch's condition. Because of this, we cannot drop the prime at ψ_t' in Eqn (7.6): to do this we must first expand ψ_t' and $\partial \psi_t'/\partial n$ in a Taylor series (3.13) in the neighborhood of faces of the cell ω . Such an expansion gives

$$P_{\text{kin}} = \frac{1}{6|\omega|K} \lim_{\varepsilon \rightarrow 0} \frac{1}{\varepsilon} \sum_t \int_{\Sigma(\omega)} dS \left\{ \psi_t^*(\mathbf{r}) \frac{\partial \psi_t'(\mathbf{r} + \varepsilon \mathbf{r}_n)}{\partial n} - \psi_t'(\mathbf{r} + \varepsilon \mathbf{r}_n) \frac{\partial \psi_t^*(\mathbf{r})}{\partial n} - \varepsilon r_n \left[\psi_t^*(\mathbf{r}) \frac{\partial^2 \psi_t'(\mathbf{r})}{\partial n^2} - \frac{\partial \psi_t'(\mathbf{r})}{\partial n} \frac{\partial \psi_t^*(\mathbf{r})}{\partial n} \right] \right\}. \quad (7.7)$$

Here the contribution with respect to $\Sigma(\omega)$ from the first two terms vanishes, since ψ_t' and $\partial \psi_t'/\partial n$ are actually taken on the boundary of cell ω' , on which the function $\partial \psi_t'/\partial n$ also obviously satisfies Bloch's condition (2.2):

$$\frac{\partial \psi_t'(\mathbf{r} + \mathbf{R}_n)}{\partial n} = \frac{\partial}{\partial n} [\exp(i\mathbf{k}, \mathbf{R}_n) \psi_t'(\mathbf{r})] = \exp(i\mathbf{k}, \mathbf{R}_n) \frac{\partial \psi_t'(\mathbf{r})}{\partial n}.$$

Now we only have the contribution from square brackets, where we can drop the primes [for one thing, this will not make the total integral over the surface $\Sigma(\omega)$ equal to zero, because the contributions from the opposite faces of the cell have the same sign: the even order of the derivative, or the even number of coefficients of odd derivatives; on the other hand, the error introduced in this way will be of the order of ε^2] and get Eqn (7.4) with due account for Eqn (7.3); r_n is the distance from the center of the cell to the face over which the

integration is carried out. Since $\int_{\Sigma(\omega)} r_n dS = 3|\omega|$, the quantity $P_{\text{kin}}^{\text{HF}}$ can again be regarded as the result of averaging over the surface of the cell with weight r_n :

$$P_{\text{kin}}^{\text{HF}}(\mathbf{r}) = [P_{\text{kin}}(\mathbf{r})]^{\text{HF}} = \frac{1}{2} \left(\frac{\partial^2}{\partial n \partial n'} - \frac{\partial^2}{2\partial n^2} - \frac{\partial^2}{2\partial n'^2} \right) \gamma^{\text{HF}}(\mathbf{r}'|\mathbf{r}) \Big|_{\mathbf{r}'=\mathbf{r}}.$$

8. Methodological example of calculation of the kinetic pressure

To give a practical example of the application of formulas (3.18), (3.19), we give a detailed description of direct calculation of the kinetic pressure for a free electron gas at the temperature T — an electrically neutral mix of nuclei (ions) and electrons in a thermostat of volume Ω . The system is constructed in such a way that no electron experiences the action of force from the side of other particles; this requires that the mean self-consistent electric field in the thermostat should be equal to zero. The FODM in this case can be represented by the hot matrix (5.8), where the normalized one-electron functions are

$$\varphi_{\mathbf{k}\alpha}(x) \equiv \psi_{\mathbf{k}}(\mathbf{r}) S_{\alpha}(\sigma) = \frac{1}{\Omega^{1/2}} \exp(i\mathbf{k}\mathbf{r}) S_{\alpha}(\sigma). \quad (8.1)$$

Then the one-electron matrix is

$$\begin{aligned} \gamma(x'|x) &\equiv \gamma(\mathbf{r}'\sigma'|\mathbf{r}\sigma) \\ &= \frac{1}{\Omega} \sum_{\mathbf{k}} n_{\mathbf{k}} \exp[i\mathbf{k}(\mathbf{r} - \mathbf{r}')] \sum_{\alpha} S_{\alpha}^*(\sigma') S_{\alpha}(\sigma) \\ &= \frac{1}{\Omega} \sum_{\mathbf{k}} n_{\mathbf{k}} \exp[i\mathbf{k}(\mathbf{r} - \mathbf{r}')] \delta_{\sigma\sigma'}. \end{aligned} \quad (8.2)$$

Equation (3.18) features the spinless FODM, which has already been 'integrated' with respect to *all* spin coordinates. It can be easily found from Eqn (8.2):

$$\gamma(\mathbf{r}'|\mathbf{r}) = \frac{2}{\Omega} \sum_{\mathbf{k}} n_{\mathbf{k}} \exp[i\mathbf{k}(\mathbf{r} - \mathbf{r}')]. \quad (8.3)$$

This function is real, since $n_{-\mathbf{k}} = n_{\mathbf{k}}$ because $\varepsilon_{-\mathbf{k}} = \varepsilon_{\mathbf{k}} \equiv \mathbf{k}^2/2$ (in the atomic system of units). Now we calculate $P_{\text{kin}}(\mathbf{r})$ from Eqn (3.18). To do this, we can divide the entire volume Ω into cells ω of cubic shape with edge b , and calculate the value of (3.18) on the faces of one such cell. Let the center of this cube be selected as the origin of coordinates x, y, z . Then this cube (known as Wigner–Seitz cell) can be described analytically by the condition $-b/2 \leq x, y, z \leq b/2$, or by the equations

$$\begin{aligned} |x+y| + |x-y| &\leq b, & |x+z| + |x-z| &\leq b, \\ |y+z| + |y-z| &\leq b. \end{aligned} \quad (8.3a)$$

The Wigner–Seitz cell (WSC) in the lattice of the crystal, and the first Brillouin zone (FBZ) in its inverse lattice are constructed in the same way: from an arbitrary point of the lattice straight lines are drawn to all its closest neighbors, and then each line is divided in half by a perpendicular plane. Then the WSC or FBZ is represented by a polyhedron bounded by these planes around the selected lattice point, which thus becomes the center of the cell.

The operator from Eqn (3.18) will retain a constant direction of differentiation for each face of the cube. Accordingly, it can be represented as the sum $\hat{D} \equiv (\hat{D}_x^+ + \hat{D}_x^-) + (\hat{D}_y^+ + \hat{D}_y^-) + (\hat{D}_z^+ + \hat{D}_z^-)$, and this operator will act upon the exponential

$$\exp\left\{i[k_x(x - x') + k_y(y - y') + k_z(z - z')]\right\}.$$

Now we can easily get

$$\begin{aligned} \hat{D}_x^+ \exp\{\dots\} \Big|_{\mathbf{r}'=\mathbf{r}} &\equiv \frac{1}{2} \left(\frac{\partial^2}{\partial x \partial x'} - \frac{\partial^2}{2\partial x^2} - \frac{\partial^2}{2x'^2} \right) \exp\{\dots\} \Big|_{\mathbf{r}'=\mathbf{r}} \\ &= k_x^2 \exp\{\dots\} \Big|_{\mathbf{r}'=\mathbf{r}} = k_x^2 \end{aligned} \quad (8.4)$$

for the right-hand x -face of the cube. For the left-hand x -face we get the same result, $\hat{D}_x^- \exp\{\dots\} \Big|_{\mathbf{r}'=\mathbf{r}} = k_x^2$, because not only the direction of the outward normal is reversed, but the direction of the vector $(\mathbf{r} - \mathbf{r}')$ as well, while vector \mathbf{k} remains the same. So we get $(\hat{D}_x^+ + \hat{D}_x^-) \exp\{\dots\} \Big|_{\mathbf{r}'=\mathbf{r}} = 2k_x^2$. Similar results are obtained for other faces of the cube:

$$\begin{aligned} (\hat{D}_y^+ + \hat{D}_y^-) \exp\{\dots\} \Big|_{\mathbf{r}'=\mathbf{r}} &= 2k_y^2, \\ (\hat{D}_z^+ + \hat{D}_z^-) \exp\{\dots\} \Big|_{\mathbf{r}'=\mathbf{r}} &= 2k_z^2. \end{aligned}$$

Then Eqn (3.18), given that $|\mathbf{R}_g - \mathbf{R}_{g'}| = b$, $|\omega| = b^3$, becomes

$$\begin{aligned} P_{\text{kin}} &= \frac{1}{6b^3} \frac{4b}{\Omega} \sum_{\mathbf{k}} n_{\mathbf{k}} \left[k_x^2 \int_{S_x} dS + k_y^2 \int_{S_y} dS + k_z^2 \int_{S_z} dS \right] \\ &= \frac{2}{3b^2} \frac{1}{\Omega} \sum_{\mathbf{k}} n_{\mathbf{k}} b^2 [k_x^2 + k_y^2 + k_z^2] = \frac{2}{3} \frac{1}{\Omega} \sum_{\mathbf{k}} n_{\mathbf{k}} k^2. \end{aligned} \quad (8.5)$$

Now we can go over from summation over the values of vector \mathbf{k} assumed within the limits of FBZ (which currently is also a cube defined in the system of coordinates k_x, k_y, k_z by relations of the type of (8.3a) if its center coincides with the origin: $-\pi/b \leq k_x, k_y, k_z \leq \pi/b$, or equations $|k_x + k_y| + |k_x - k_y| \leq 2\pi/b$, $|k_x + k_z| + |k_x - k_z| \leq 2\pi/b$, $|k_y + k_z| + |k_y - k_z| \leq 2\pi/b$) to integration with respect to its values, or with respect to the values of energy $\varepsilon = \varepsilon(\mathbf{k}) \equiv \varepsilon_{\mathbf{k}}$, corresponding to these values of vector \mathbf{k} , using the known relations

$$\frac{1}{\Omega} \sum_{\mathbf{k}} \Big|_{\Omega \rightarrow \infty} \Rightarrow \int_{\omega_{\mathbf{k}}} \frac{d\mathbf{k}}{(2\pi)^3} \Rightarrow \int_{\varepsilon_1(\Omega)}^{\varepsilon_2(\Omega)} \rho(\varepsilon, \Omega) d\varepsilon, \quad (8.6a)$$

$$\frac{1}{K} \sum_{\mathbf{k}} \Big|_{K \rightarrow \infty} \Rightarrow \int_{\omega_{\mathbf{k}}} \frac{d\mathbf{k}}{|\omega_{\mathbf{k}}|} \Rightarrow \int_{\varepsilon_1(K)}^{\varepsilon_2(K)} \rho(\varepsilon, K) d\varepsilon, \quad (8.6b)$$

since $\Omega = K|\omega_r| = Kb^3$; $|\omega_r \omega_{\mathbf{k}}| = b^3|\omega_{\mathbf{k}}| = (2\pi)^3$, where $\omega_{\mathbf{k}} \equiv$ FBZ and ω_r are figures, and $|\omega_{\mathbf{k}}|$ and $|\omega_r|$ their volumes; $\rho(\varepsilon)$ is the density of the energy one-electron states, or the *Jacobian* of transition from integration variable \mathbf{k} to integration variable $\varepsilon_{\mathbf{k}}$; K is the total number of cells in such a crystal.

So, for the kinetic pressure we get the expression

$$\begin{aligned} P_{\text{kin}} &= \frac{2}{3} \frac{1}{\Omega} \sum_{\mathbf{k}} n_{\mathbf{k}} k^2 = \frac{2}{3} \int_{\omega_{\mathbf{k}}} \frac{d\mathbf{k}}{(2\pi)^3} n_{\mathbf{k}} k^2 \\ &= \frac{2}{3} \int_{-\pi/b}^{\pi/b} \frac{dk_x}{2\pi} \int_{-\pi/b}^{\pi/b} \frac{dk_y}{2\pi} \int_{-\pi/b}^{\pi/b} \frac{dk_z}{2\pi} n_{\mathbf{k}} (k_x^2 + k_y^2 + k_z^2), \end{aligned} \quad (8.7)$$

where $n_{\mathbf{k}} \equiv 1/\{\exp[\beta(\varepsilon_{\mathbf{k}} - \varepsilon_F)] + 1\}$, $\varepsilon_{\mathbf{k}} = k^2/2$, $\varepsilon_F = k_F^2/2$, $\beta \equiv 1/(k_B T)$, k_B is the Boltzmann constant, and ε_F is the Fermi energy, from which the one-electron energies $\varepsilon_{\mathbf{k}}$ are counted in the formula for $n_{\mathbf{k}}$. This energy separates the *throughout-occupied* energy states from the *throughout-vacant* states. Such a sharp division can only exist in a free electron gas, and only at zero temperature. The existence of even a slight force field will blur this boundary. At a finite temperature such blurring will take place even in the case of a free electron gas — it is the temperature blurring of the boundary. In the general case the blurring is caused both by the force field and by the temperature. In this connection we should recall the relation between the mean thermal energy of free electrons in metal at room temperature ($T \approx 300^\circ\text{K}$), which is of the order of $k_B T \approx 0.03$ eV, and the typical Fermi energy for metals $\varepsilon_F \approx 3-5$ eV. Their ratio is $\varepsilon_F/(k_B T) > 100$, and therefore there is almost no temperature blurring in metals. For $\varepsilon_{\mathbf{k}} = \varepsilon_F$, irrespective of the temperature, we get $n_{\mathbf{k}} = 1/2$ — this means that ε_F is the one-electron energy level whose occupancy does not depend on the temperature and is always equal to $1/2$. By the very essence of $n_{\mathbf{k}}$, we have the relation $\sum_{\mathbf{k}} n_{\mathbf{k}} = N_{\text{cp}}$ — that is, ε_F depends on the total number of free electrons of the metal N . In those cases when N is subject to change, it is convenient to replace $\varepsilon_F(N)$ with the chemical potential of electrons $\mu(N, T)$, and then we get the dependence $N = N(T, \mu)$. The parameter μ , calculated or eliminated from the final results, is based on the requirement $N_{\text{cp}} \equiv \sum_{\mathbf{k}} n_{\mathbf{k}} = N$; the value of N is then set. The chemical potential for any T and given N satisfies the condition $\mu(T, N) \leq \varepsilon_F(T=0, N)$, where the equals sign corresponds to $T=0$. Graphically [in the plane $\varepsilon, f(\varepsilon)$], the location of μ at given temperature T corresponds to that value of $\varepsilon = \varepsilon_0$ (that is, $\mu = \varepsilon_0$) at which $f(\varepsilon_0) = 1/2$; here $f(\varepsilon)$ is the Fermi energy distribution of electrons. By shifting the reference point $\varepsilon_{\mathbf{k}}$ — that is, by making replacements like $\varepsilon_{\mathbf{k}} \rightarrow \varepsilon'_{\mathbf{k}} = \varepsilon_{\mathbf{k}} - \varepsilon_F$, or $\varepsilon_{\mathbf{k}} \rightarrow \varepsilon''_{\mathbf{k}} = \varepsilon_{\mathbf{k}} - \mu$, it is possible to avoid dealing with small differences $\varepsilon_{\mathbf{k}'} - \varepsilon_{\mathbf{k}}$ of large values $\varepsilon_{\mathbf{k}'}$ and $\varepsilon_{\mathbf{k}}$, as opposed to the differences $\varepsilon'_{\mathbf{k}'} - \varepsilon'_{\mathbf{k}}$ which are of the same order as $\varepsilon'_{\mathbf{k}'}$ and $\varepsilon'_{\mathbf{k}}$. Of course, the differences as such remain the same: $\varepsilon'_{\mathbf{k}'} - \varepsilon'_{\mathbf{k}} = \varepsilon_{\mathbf{k}'} - \varepsilon_{\mathbf{k}}$. Finally, the equality $\varepsilon_F^+ = \varepsilon_F^-$, which holds for equilibrium of the system of electrons with spin (+) and (-) at $T=0$, is replaced with $\mu^+ = \mu^-$ in the case of $T \neq 0$ (the condition of phase equilibrium in a one-component, say, two-phase system is $T' = T, P' = P, \mu' = \mu$; if the phases of the system *beforehand* have the same T and P , then the three foregoing conditions of phase equilibrium can be replaced with one condition $\mu'(T, P) = \mu(T, P)$, which was earlier expressed in the form $\mu^+ = \mu^-$. As a matter of fact, the condition $\mu'(T, P) = \mu(T, P)$ has the form of relations $P = P(T)$ or $T = T(P)$, which define the curves of phase equilibrium of the system in the planes T, P or P, T , respectively. Unfortunately, the particular form of the functions $\mu'(T, P)$ and $\mu(T, P)$ is usually not known, and therefore it is not possible to express $P = P(T)$ or $T = T(P)$ from the equation $\mu' = \mu$. At the same time, it is easy to find the differential form (dP/dT or dT/dP) of curves $P = P(T)$ or $T = T(P)$ from $d\mu' = d\mu$ with due account for $d\mu = -SdT + VdP$. This will bring us to the Clapeyron–Clausius equation $dP/dT = \lambda/[(V - V')T]$, where $\lambda \equiv (S - S')T$ is the heat of transition from one phase to the other). However, the particular values of μ by themselves do not define the actual distribution of electrons with respect to energy levels, as opposed to ε_F . In practical calculations, $\sum_{\mathbf{k}} n_{\mathbf{k}} = N$ is usually replaced with

$(1/N) \sum_{\mathbf{k}} n_{\mathbf{k}} = 1/N \equiv n$, where n is the number of free electrons per cell of the metal; then ε_F and μ show their natural dependence on the concentration (density) of free electrons in the metal: $\varepsilon_F(T=0, n)$ and $\mu(T, n)$.

Integration in Eqn (8.7) is carried out with respect to the entire volume of FBZ, since at $T \neq 0$ any \mathbf{k} state within the FBZ can be occupied with the probability $0 \leq n_{\mathbf{k}} \leq 1$. At $T = 0$, the integration with respect to \mathbf{k} must be carried out up to k_F : $0 \leq |\mathbf{k}| \leq k_F$. At $T = 0$ expression (8.7) becomes much simpler (in the atomic system of units):

$$\begin{aligned} P_{\text{kin}} &= \frac{2}{3} \int_{|\mathbf{k}| \leq k_F} \frac{d\mathbf{k}}{(2\pi)^3} k^2 \\ &= \frac{2}{3} \int_0^{2\pi} d\varphi \int_0^\pi \sin \vartheta d\vartheta \int_0^{k_F} \frac{k^2 dk}{(2\pi)^3} k^2 \\ &= \frac{2}{3} 4\pi \int_0^{k_F} \frac{k^4 dk}{(2\pi)^3} = \frac{k_F^5}{15\pi^2} = \frac{2}{3} \frac{E_{\text{kin}}}{\Omega}. \end{aligned} \quad (8.8)$$

Since the Fermi quasi-momentum of the electron is given by [58] $k_F = (3\pi^2 N/\Omega)^{1/3}$, where N is the number of electrons, Eqn (8.8) assumes its conventional form [44]:

$$P_{\text{kin}} = \frac{k_F^5}{15\pi^2} = \frac{1}{5} (3\pi^2)^{2/3} \left(\frac{N}{\Omega} \right)^{5/3}. \quad (8.9)$$

Finally, to apply the finishing touch to this section, we must give at least a brief description of the analytical methods for calculating the function $\rho(\varepsilon)$ — the number of one-electron energy states per unit energy. This function, apart from its being the Jacobian of the transition from integration with respect to \mathbf{k} to integration over $\varepsilon_{\mathbf{k}}$ [see Eqn (8.6)], is quite useful in studying the low-lying excited one-particle states of the crystal, located in the region of \mathbf{k} space close to the Fermi surface. In \mathbf{k} space these states are distributed uniformly [$\rho(\mathbf{k}) = \text{const}$], while their distribution in the ε space is not uniform [$\rho(\varepsilon) \neq \text{const}$]. For the atomic level, the number of such states is given by the order of degeneracy, or, which is the same, by the statistical weight of the level. In the case of s, p, d levels (most often encountered in applications — they correspond to $l = 0, 1, 2$), their statistical weights are $g = 2, 6, 10$, respectively. In crystals these levels become bands of the same names, and with the same order of degeneracy for each value of \mathbf{k} in the band. The number of occupied (throughout) states per lattice point is given by

$$n = \frac{g}{K} \sum_{\mathbf{k}} l_{\mathbf{k}} = g \int_{\omega} \frac{d\mathbf{k}}{|\omega_{\mathbf{k}}|}, \quad 0 \leq |\mathbf{k}| \leq k_F, \quad (8.10)$$

where K is the number of cells (or points) in the lattice.

To calculate $\rho(\varepsilon)$, corresponding to some band $\varepsilon_{\mathbf{k}}$, one may use its straightforward definition [31],

$$\rho(\varepsilon) \equiv \frac{dN}{d\varepsilon} = \frac{d}{d\varepsilon} \left[\frac{g\Omega}{(2\pi)^3} \int d\mathbf{k} \right] = g \frac{d}{d\varepsilon} \int_{\omega} \frac{d\mathbf{k}}{|\omega_{\mathbf{k}}|}, \quad (8.11)$$

which is usually, however, represented in a different form [31]:

$$\rho(\varepsilon) \equiv \frac{g\Omega}{(2\pi)^3} \int \frac{dS}{|\nabla_{\mathbf{k}} \varepsilon_{\mathbf{k}}|} = g \frac{1}{|\omega_{\mathbf{k}}|} \int \frac{dS}{|\nabla_{\mathbf{k}} \varepsilon_{\mathbf{k}}|}. \quad (8.12)$$

The integral in Eqn (8.12) is taken over the volume of \mathbf{k} space bounded by the isoenergetic surface (IES), corresponding to the energy $\varepsilon_{\mathbf{k}}$ equal to ε , while in Eqn (8.12) the integral is

taken over the isoenergetic surface itself (Ω is the volume of crystal). The integral in Eqn (8.12) is always taken within *one* energy band, irrespective of whether the surface is closed or not.

Sometimes the desired result can be found from the simple identity [52]

$$\begin{aligned} \rho(\varepsilon) &\equiv \frac{g}{N} \sum_{\mathbf{k}} \delta(\varepsilon - \varepsilon_{\mathbf{k}}) = g \int_{\omega_{\mathbf{k}}} \frac{d\mathbf{k}}{|\omega_{\mathbf{k}}|} \delta(\varepsilon - \varepsilon_{\mathbf{k}}) \\ &= g \int_{-\infty}^{+\infty} \frac{dx}{2\pi} \exp(\pm ix\varepsilon) \int_{\omega_{\mathbf{k}}} \frac{d\mathbf{k}}{|\omega_{\mathbf{k}}|} \exp(\mp ix\varepsilon_{\mathbf{k}}). \end{aligned} \quad (8.13)$$

Finally, one may use the two-point the Green function of the crystal

$$\begin{aligned} G_{jj'}(z) &\equiv \frac{1}{K} \sum_{\mathbf{k}} \frac{\exp[i\mathbf{k}(\mathbf{R}_j - \mathbf{R}_{j'})]}{z - \varepsilon_{\mathbf{k}}} \\ &= \frac{1}{K} \sum_{\mathbf{k}} \exp[i\mathbf{k}(\mathbf{R}_j - \mathbf{R}_{j'})] G_{\mathbf{k}}(z), \end{aligned} \quad (8.14)$$

since with $j' = j$ (then $G_{jj'}$ becomes a one-point function G_{jj} which does not depend on the cell number) its imaginary part is equal to $\rho(\varepsilon)$. Indeed, doing some simple algebra we get

$$\begin{aligned} G_{jj}(z) &\equiv \frac{1}{K} \sum_{\mathbf{k}} \frac{1}{z - \varepsilon_{\mathbf{k}}} \rightarrow G_{jj}(\varepsilon) = \lim_{\varepsilon' \rightarrow +0} \left(\frac{1}{K} \sum_{\mathbf{k}} \frac{1}{\varepsilon - \varepsilon_{\mathbf{k}} \pm i\varepsilon'} \right) \\ &= \frac{1}{K} \sum_{\mathbf{k}} \frac{\text{V.p.}}{\varepsilon - \varepsilon_{\mathbf{k}}} \mp i\pi \frac{1}{K} \sum_{\mathbf{k}} \delta(\varepsilon - \varepsilon_{\mathbf{k}}) \\ &= \frac{1}{K} \sum_{\mathbf{k}} \frac{\text{V.p.}}{\varepsilon - \varepsilon_{\mathbf{k}}} \mp i\pi \rho(\varepsilon), \end{aligned} \quad (8.15)$$

and see that the use of Green function leads us to Eqn (8.13). All this can be found by integration

$$\begin{aligned} G_{jj}(z) &\equiv \frac{1}{K} \sum_{\mathbf{k}} \frac{1}{z - \varepsilon_{\mathbf{k}}} = \int_{\omega_{\mathbf{k}}} \frac{d\mathbf{k}}{|\omega_{\mathbf{k}}|} \frac{1}{z - \varepsilon_{\mathbf{k}}} = \int \rho(\varepsilon'') \frac{d\varepsilon''}{z - \varepsilon''} \\ &\rightarrow G_{jj}(\varepsilon) = \lim_{\varepsilon' \rightarrow +0} \left[\int \rho(\varepsilon'') \frac{d\varepsilon''}{\varepsilon - \varepsilon'' \pm i\varepsilon'} \right] \\ &= \text{V.p.} \int \rho(\varepsilon'') \frac{d\varepsilon''}{\varepsilon - \varepsilon''} \mp i\pi \int \rho(\varepsilon'') \delta(\varepsilon - \varepsilon'') d\varepsilon'' \\ &= \text{V.p.} \int \rho(\varepsilon'') \frac{d\varepsilon''}{\varepsilon - \varepsilon''} \mp i\pi \rho(\varepsilon). \end{aligned} \quad (8.16)$$

In Eqns (8.15), (8.16) we have used the computational limit

$$\lim_{\varepsilon' \rightarrow +0} \frac{1}{\varepsilon - \varepsilon_{\mathbf{k}} \pm i\varepsilon'} \equiv \frac{\text{V.p.}}{\varepsilon - \varepsilon_{\mathbf{k}}} \mp i\pi \delta(\varepsilon - \varepsilon_{\mathbf{k}}). \quad (8.17)$$

This identity is easily proved by straightforward integration of both its parts. In practice it just means that *in the integrand* the left-hand side of Eqn (8.17) can be replaced with its right-hand side.

Unfortunately — and this applies to all three methods — practical calculation of $\rho(\varepsilon)$ is usually associated with great mathematical and technical difficulties. Two simple examples of calculation of $\rho(\varepsilon)$ are given below.

(a) Free electron gas. Here $g = 2$, and we also may set $\varepsilon_{\mathbf{k}} = \mathbf{k}^2/2$; then the isoenergetic surfaces are spheres

$k_x^2 + k_y^2 + k_z^2 = k^2$. In a spherical system of coordinates (k, ϑ, φ) the element of volume of a sphere of radius k is $d\Omega = k^2 dk d\Phi$, and its surface element is $dS = k^2 d\Phi$, where $d\Phi \equiv \sin \vartheta d\vartheta d\varphi$ is the solid angle increment.

According to Eqn (8.11),

$$\rho(\varepsilon) = \frac{d}{d\varepsilon} \left[\frac{g\Omega}{(2\pi)^3} \int d\mathbf{k} \right] = \frac{g\Omega}{(2\pi)^3} 4\pi \frac{d}{d\varepsilon} \frac{k^3}{3} = \frac{\Omega}{\pi^2} (2\varepsilon)^{1/2}.$$

When Eqn (8.12) is used, the modulus of gradient $|\nabla_{\mathbf{k}}\varepsilon_{\mathbf{k}}| = k$ is calculated first (the polar and azimuthal projections of $\nabla_{\mathbf{k}}\varepsilon_{\mathbf{k}}$ are zero), and then we get

$$\begin{aligned} \rho(\varepsilon) &= \frac{g\Omega}{(2\pi)^3} \int \frac{dS}{|\nabla_{\mathbf{k}}\varepsilon_{\mathbf{k}}|} = \frac{g\Omega}{(2\pi)^3} k \int d\Phi \\ &= \frac{g\Omega}{(2\pi)^3} k 4\pi = \frac{\Omega}{\pi^2} (2\varepsilon)^{1/2}. \end{aligned}$$

By Eqn (8.13), the integral is nonanalytical.

(b) In connection with the studies of high-temperature superconductivity, much used these days are two-dimensional (in particular, square) lattices with a dispersion law of free electrons like

$$\varepsilon_{\mathbf{k}} = -t(\cos k_x + \cos k_y), \tag{8.18}$$

where t is the energy of electron transition to the closest adjacent lattice point. Usually it is assumed that the band (8.18) arises from the s level of the free atom, and therefore $t > 0$ and $g = 2$. The FBZ of such a lattice in coordinates (k_x, k_y) is a square defined by the condition $-\pi \leq k_x, k_y \leq \pi$ (or equation $|k_x + k_y| + |k_x - k_y| \leq 2\pi$, if the side of square of \mathbf{r} lattice is equal to one, see Fig. 1). In this diagram, the FBZ is shown by a dashed line, and the IE lines are solid. We see that the IE line $|k_x| + |k_y| = \pi$ (which corresponds to $\varepsilon_{\mathbf{k}} = 0$) separates the IE lines with $\varepsilon_{\mathbf{k}} = \text{const} < 0$ (they are located inside the region confined by this line, and are all closed within the limits of the FBZ) from the IE lines with $\varepsilon_{\mathbf{k}} = \text{const} > 0$ (they fall outside of a region confined by this line, and are not closed within the limits of the FBZ). The IE line $\varepsilon_{\mathbf{k}} = \text{const} = C_1$ passes through a given point (k_{x0}, k_{y0}) if

$\varepsilon_{\mathbf{k}}(k_{x0}, k_{y0}) = C_1$. All other points belonging to this IE line are found from the solution of equation $\varepsilon_{\mathbf{k}} = C_1$ with respect to k_y for given k_x (or vice versa). The area of the square delimited by the 'zero' IE line is half the area of the FBZ, and therefore it corresponds to the halfway occupation of the zone ($n = 1$). The modulus of gradient $\varepsilon_{\mathbf{k}}$ for Eqn (8.18) is

$$|\nabla_{\mathbf{k}}\varepsilon_{\mathbf{k}}| = t(\sin^2 k_x + \sin^2 k_y)^{1/2}. \tag{8.19}$$

To calculate $\rho(\varepsilon)$, the two-dimensional analogue of Eqn (8.12) must be integrated along some IE line. Analytically, this is best done along the 'zero' IE line. Then the surface integral in Eqn (8.12) becomes a path integral

$$\begin{aligned} \rho(\varepsilon) &= \frac{gS}{(2\pi)^2} \int \frac{dl}{|\nabla_{\mathbf{k}}\varepsilon_{\mathbf{k}}|} = \frac{gS}{(2\pi)^2 t} \int (\sin^2 k_x + \sin^2 k_y)^{-1/2} dl \\ &= \frac{gS}{(2\pi)^2 t} \int |\sin k_x|^{-1} dk_x \\ &= \frac{gS}{(2\pi)^2 t} \left[2 \int_0^\pi (\sin k_x)^{-1} dk_x - 2 \int_{-\pi}^0 (\sin k_x)^{-1} dk_x \right]. \end{aligned} \tag{8.20}$$

Here the integration of function $1/|\nabla_{\mathbf{k}}\varepsilon_{\mathbf{k}}|$ is carried out along the line $|k_x| + |k_y| = \pi$, and we use the relationship $dl = (dk_x^2 + dk_y^2)^{1/2} = dk_x(1 + dk_y^2/dk_x^2)^{1/2}$. We see that the integral (8.20) does not exist in the ordinary sense. It could have existed in the sense of its principal value, because the areas hatched in the same way in Fig. 2 might balance out. This is not the case, however, and integral (8.20) diverges. Analytically it looks like this:

$$\begin{aligned} &\lim_{\varepsilon_1, \varepsilon_2 \rightarrow 0} \left[2 \int_{\varepsilon_1}^{\pi - \varepsilon_2} (\sin k_x)^{-1} dk_x - 2 \int_{-\pi + \varepsilon_2}^{-\varepsilon_1} (\sin k_x)^{-1} dk_x \right] \\ &= \lim_{\varepsilon_1, \varepsilon_2 \rightarrow 0} \left(2 \ln \left| \tan \frac{\pi - \varepsilon_2}{2} \right| - 2 \ln \left| \tan \frac{\varepsilon_1}{2} \right| \right. \\ &\quad \left. + 2 \ln \left| \tan \frac{\pi - \varepsilon_2}{2} \right| - 2 \ln \left| \tan \frac{\varepsilon_1}{2} \right| \right) \\ &= 4 \lim_{\varepsilon_1, \varepsilon_2 \rightarrow 0} \ln \left| \frac{\tan[(\pi - \varepsilon_2)/2]}{\tan(\varepsilon_1/2)} \right| \rightarrow \infty, \end{aligned} \tag{8.21}$$

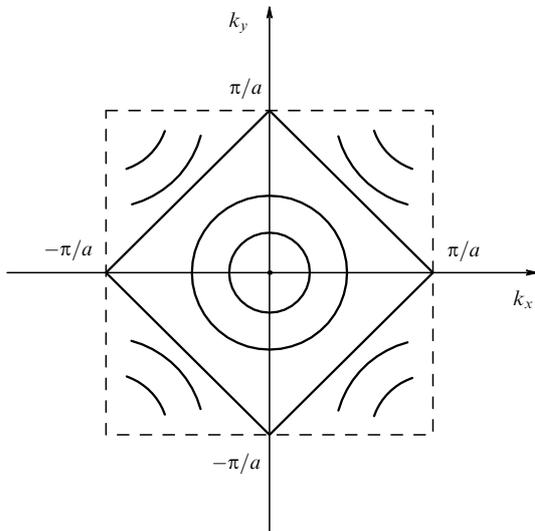


Figure 1.

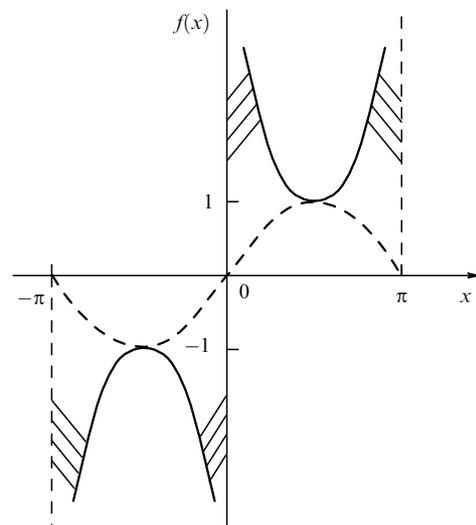


Figure 2.

and the density of the one-electron energy states on the isoenergetic line $\epsilon_{\mathbf{k}} = 0$ actually diverges.

9. Thermodynamic theory of the equation of state of matter

Staying within the framework of thermodynamics, it is not possible to express the *equation* for calculating the thermodynamic parameters of matter. This cannot be done even for the most simple thermodynamic system — the ideal gas with constant heat capacity $(\partial E/\partial T)_V = \text{const}$ (perfect gas), because thermodynamics can only give us the thermodynamic *identities* that express the linkage between the thermodynamic parameters of the system in question. For example, the identity

$$dE_c(V, T=0) = -P_c(V, T=0) dV, \quad (9.1)$$

which holds for any cold system, allows calculation, for example, of the internal cold energy $E_c(V)$ [or the cold pressure $P_c(V)$] only if the function of cold pressure $P_c(V)$ [or $E_c(V)$] is known from *nonthermodynamic* sources. It is only then that we can integrate the identity (9.1) and find the solution for $E_c(V)$:

$$E_c(V) = E_c(V_0) - \int_1^2 P_c(V) dV, \quad 1 \equiv V_0, \quad 2 \equiv V \quad (9.2)$$

[the pressure is found by differentiating $E_c(V)$]. The necessity to obtain information from non-thermodynamic sources is the main reason why statistical physics gets involved. As a result, thermodynamic functions of matter are expressed in terms of purely statistical concepts — for example, via the two-particle distribution functions $n_2(r)$ [45, 60]:

$$E(V, T) = \frac{3}{2} RT + \frac{V}{2} \int U(r) n_2(r) 4\pi r^2 dr, \quad (9.3)$$

$$VP(V, T) = RT - \frac{V}{6} \int r \frac{\partial U(r)}{\partial r} n_2(r) 4\pi r^2 dr. \quad (9.4)$$

These formulas are suitable for describing the classical systems (that is, such systems whose kinetic energy can be identified with the kinetic energy of random motion of their particles), if the law of two-particle interaction of their structural elements (electrons, atoms, ...) and the two-particle distribution function are known and can be represented in the form

$$U(\mathbf{r}_1, \mathbf{r}_2) \rightarrow U(|\mathbf{r}_1 - \mathbf{r}_2|), \quad n_2(\mathbf{r}_1, \mathbf{r}_2) \rightarrow n_2(|\mathbf{r}_1 - \mathbf{r}_2|). \quad (9.5)$$

Thus, for the thermodynamic description of such systems one only needs to know $U(r)$ and $n_2(r)$. In practice, however, even a very approximate calculation of $n_2(r)$ turns out to be a quite formidable task.

The approach described below leads to purely thermodynamic differential (or, if desired, integro-differential) *equations* for the pressure $P(V, T)$ and internal energy $E(V, T)$ of the thermodynamic system under consideration — that is, the problem of calculation of $P(V, T)$ and $E(V, T)$ is reduced to solving the initial problem of mathematical physics (the Cauchy problem) [59]. The idea of this approach [43] consists in transforming the identity

$$T \left(\frac{\partial P}{\partial T} \right)_V = \left(\frac{\partial E}{\partial V} \right)_T + P(V, T), \quad (9.6)$$

which connects two thermodynamic functions of the system (internal energy and pressure), into a differential equation for one of these functions, through the use of such sources as may furnish the partial derivatives occurring in Eqn (9.6).

(a) One such relation, commonly used in the theory of the EOS of matter, is the purely phenomenological linkage between thermal pressure in the system and its thermal energy:

$$P_{\text{th}}(V, T) = \Gamma(V) \frac{E_{\text{th}}(V, T)}{V}, \quad (9.7)$$

proposed by Mie and Grueneisen [61, 62]. From this equality one may express both the derivative $(\partial E_{\text{th}}/\partial V)_T$ and the derivative $(\partial P_{\text{th}}/\partial T)_V$, to substitute them (one at a time!) into the thermal counterpart of identity (9.6) [43]:

$$T \left(\frac{\partial P_{\text{th}}}{\partial T} \right)_V = \left(\frac{\partial E_{\text{th}}}{\partial V} \right)_T + P_{\text{th}}(V, T) \quad (9.7a)$$

so as to express the equations in $P_{\text{th}}(V, T)$ or $E_{\text{th}}(V, T)$, respectively:

$$\begin{aligned} \left(\frac{\partial \ln P_{\text{th}}}{\partial \ln T} \right)_V - \frac{1}{\Gamma(V)} \left(\frac{\partial \ln P_{\text{th}}}{\partial \ln V} \right)_{T \neq 0} &= \varkappa(V), \\ \left(\frac{\partial \ln E_{\text{th}}}{\partial \ln T} \right)_V - \frac{1}{\Gamma(V)} \left(\frac{\partial \ln E_{\text{th}}}{\partial \ln V} \right)_{T \neq 0} &= 1, \end{aligned} \quad (9.8)$$

where $\varkappa(V) \equiv (\Gamma + \Gamma^2 - d\Gamma/d \ln V)/\Gamma^2$.

For unambiguous solution of these equations it is necessary to define $\Gamma(V)$ and set the boundary conditions $P_{\text{th}}(V, T_0) \equiv f(V)$ or $P_{\text{th}}(V_0, T) \equiv \varphi(T)$, where $f(V)$ and $\varphi(T)$ are known functions (for example, taken from experiment or from other considerations). Similar conditions must also be defined when solving the equation for $E_{\text{th}}(V, T)$. Equations (9.8) can be written in the integro-differential form

$$\begin{aligned} P_{\text{th}}(V, T) &= P_{\text{th}}(V, T_0) + \left[\varkappa(V) + \frac{1}{\Gamma} \frac{\partial}{\partial \ln V} \right] \int_1^2 P_{\text{th}}(V, x) \frac{dx}{x}, \\ E_{\text{th}}(V, T) &= E_{\text{th}}(V, T_0) + \left(1 + \frac{1}{\Gamma} \frac{\partial}{\partial \ln V} \right) \int_1^2 E_{\text{th}}(V, x) \frac{dx}{x}, \\ 1 \equiv T_0, \quad 2 \equiv T. \end{aligned} \quad (9.8a)$$

The resulting $P_{\text{th}}(V, T)$ and $E_{\text{th}}(V, T)$ must be supplemented by their cold parts $P_c(V)$, $E_c(V)$ to obtain the total functions $P(V, T)$, $E(V, T)$:

$$\begin{aligned} P(V, T) &= P_c(V, T=0) + P_{\text{th}}(V, T), \\ E(V, T) &= E_c(V, T=0) + E_{\text{th}}(V, T). \end{aligned} \quad (9.9)$$

It ought to be noted that decompositions like Eqn (9.9) are clear-cut only in the case of *smooth* (static) processes [59], when linkages similar to Eqn (9.1) are used for the cold parts.

(b) The virial theorem could be used for another non-thermodynamic relation [43, 59]; its general drawback, however, is that, in addition to the total internal energy, it separately involves its kinetic part. In other words, in the general case the VT has the form $F(P, E, E_{\text{kin}}, V) = 0$, and this is the cause of its impracticability: this expression is apparently not suitable for expressing the *total* partial derivatives from $P(V, T)$ and $E(V, T)$, needed for substitution into Eqn (9.6), and therefore the equations will have to be written *separately* for the kinetic and potential parts of the

pressure and energy, which will create additional problems with the formulation of boundary conditions.

(c) However, for a certain class of systems (the *classical* systems [46]) the virial theorem allows derivation of the exact equations for thermodynamic functions in place of the conventional relations (9.3) and (9.4) (see Ref. [45], p. 133) that require knowing the two-particle distribution function $n_2(r)$. According to Feynman, such systems of interacting particles whose kinetic energy can be written as

$$E_{\text{kin}}(T) = \frac{RT}{\gamma - 1}, \quad (9.10)$$

are classical, that is, whose kinetic energy coincides with the kinetic energy of random motion of particles of the system, and therefore has the form of the internal energy of nonquantum ideal gas (not necessarily monoatomic). For such systems the virial theorem (3.4a) becomes

$$3VP = 3RT + \left[E(T, V) - \frac{RT}{\gamma - 1} \right] \sum_n n. \quad (9.11)$$

Hence it is easy to find the total partial isothermal derivative

$$\left(\frac{\partial E}{\partial V} \right)_T = \frac{3}{\sum_n n} \left[P + V \left(\frac{\partial P}{\partial V} \right)_T \right],$$

which is necessary for converting the identity (9.6) into the equation for pressure:

$$\left(\frac{\partial \ln P}{\partial \ln T} \right)_V - \kappa \left(\frac{\partial \ln P}{\partial \ln V} \right)_T = 1 + \kappa, \quad \kappa \equiv \frac{3}{\sum_n n}. \quad (9.12)$$

In entirely the same way we get the equation for the internal energy of classical system of particles:

$$T \left(\frac{\partial E}{\partial T} \right)_V - \kappa V \left(\frac{\partial E}{\partial V} \right)_T = E. \quad (9.13)$$

(d) Equations (9.8) and (9.12) can be solved by the method of characteristics (see Ref. [63], p. 197). For illustration we shall solve Eqn (9.13) — of course, assuming that the initial curve $E(V, T_0) \equiv f(V)$ or $E(V_0, T) \equiv \varphi(T)$ is given. For definiteness, assume that we know $f(V)$. Then, as usual, we first introduce the new variables (for example, s and t), and require that s should only change along the characteristics, and t along the initial curve [in this case this curve will be represented by the line $T = T_0$ in the plane (V, T)]. These conditions are satisfiable, because in the case of linear equations of the first order [such as Eqns (9.8) and (9.12), (9.13)] the initial conditions defined at a certain point of the axis V move in the (V, T) plane along a certain line called the characteristic. The equations of characteristics of the initial equation (9.13) have the form $dT/ds = T$, $dV/ds = -\kappa V$, and their solutions are $T(s) = T(s=0) \exp s = T_0 \exp s$, $V(s) = (s=0) \exp(-\kappa s) = t \exp(-\kappa s)$. In the (V, T) plane, the t -parametric equation of characteristics has the form

$$T = T_0 \left(\frac{V}{t} \right)^{-1/\kappa} \rightarrow t = \left(\frac{T}{T_0} \right)^\kappa V. \quad (9.14)$$

Along the characteristic (9.14), for E we get the equation $dE/ds = E$, which admits the solution

$$E(s; t) = E(s=0; t) \exp s = f(t) \exp s.$$

Accordingly, the exact solution of the initial equation (9.13) is

$$E(V, T) = f(t) \frac{T}{T_0}, \quad (9.15)$$

where the parameter t is defined by Eqn (9.14). The other two equations are solved in exactly the same way.

(e) Of special importance in the case of *adiabatic* compression ($dE = -P dV$) is the question concerning the temperature of matter reached because of compression. For a perfect gas (PG) we have exact theoretical formulas for the temperature.

Gradual (static) adiabatic compression of PG:

$$TV^{\gamma-1} = \text{const} \rightarrow T = T_0 \left(\frac{\rho}{\rho_0} \right)^{\gamma-1} = T_0 \sigma^{\gamma-1}. \quad (9.16)$$

Shock (dynamic) adiabatic compression of PG:

$$T = T_0 P' \frac{\kappa + P'}{\kappa P' + 1}, \quad \kappa = \frac{\gamma + 1}{\gamma - 1}, \quad P' \equiv \frac{P}{P_0}. \quad (9.17)$$

For the case of gradual adiabatic compression of arbitrary substance we only have the integral formula for the temperature [43, 61],

$$T = T_0 \exp \left[- \int_1^2 \left(\frac{\partial P}{\partial E} \right)_V dV \right] = T_0 \exp \left[- \int_1^2 \left(\frac{\partial P_{\text{th}}}{\partial E_{\text{th}}} \right)_V dV \right], \quad (9.18)$$

$$1 \equiv V_0, \quad 2 \equiv V,$$

and its calculation requires knowing the pressure as a function of volume and energy $P = P(V, E)$ in the static process (along the Poisson adiabat). It is only for PG that this function is known:

$$E(V, P) = \frac{VP}{\gamma - 1} \rightarrow P = \frac{E}{V}(\gamma - 1), \quad (9.19)$$

where $(\gamma - 1)$ is the Grueneisen coefficient for PG, and $P \equiv P_{\text{th}}$, $E \equiv E_{\text{th}}$. Then the isentrope (9.18) becomes (9.16), since $(\partial P_{\text{th}}/\partial E_{\text{th}})_V = (\gamma - 1)/V$. Making use of Eqn (9.7), we can simplify the isentrope (9.18):

$$T = T_0 \exp \left[- \int_1^2 \Gamma(V) \frac{dV}{V} \right], \quad 1 \equiv V_0, \quad 2 \equiv V. \quad (9.20)$$

It is important that for classical systems (according to Ref. [45]), the combination of VT (9.11) with the shock adiabat (SA) [61, 62]

$$2(E - E_0) = (P + P_0)(V_0 - V), \quad (9.21)$$

which holds for any substance in any aggregate state, allows for the purely analytical calculation of the temperature for the *shock* compression of the classical system as well — of course, given that P_{sh} and V_{sh} are known. [Incidentally, from VT (9.11) it is possible to find the linkage between $P_c(V)$ and $E_c(V)$, sufficient for closing the relation (9.1).] The energy E_{kin} in Feynman's formulas (9.3), (9.4) is $E_{\text{kin}} = (3/2)RT$, which corresponds to E_{kin} of system comprised of such structural units for which $\gamma = 5/3$. According to Feynman, this is because it is very difficult to take into account the existence of internal degrees of freedom of the elements of *condensed* classical systems. Therefore, he regards such

systems as consisting of particles of inert gas. If we set $\gamma = 5/3$, and use a purely Coulombian potential (setting $\sum_n n = 1$), then VT (9.11) assumes a very simple form

$$6PV = 2E + 3RT. \quad (9.21a)$$

Combining this relation with SA (9.21), we may get

$$T_{\text{sh}} - T_0 = (7V_{\text{sh}} - V_0) \frac{P_{\text{sh}}}{3R}, \quad (9.22)$$

where the values of P_{sh} and V_{sh} are taken from experiment, $V_0 = 10^{-6}(\mu/\rho) \text{ m}^3$ is the molar volume of substance, μ is the molar mass in g mol^{-1} (numerically equal to the molecular mass of the substance), ρ is the normal density of substance in grams per cm^3 , $R = 8.31 \text{ J (mol K)}^{-1}$, $T_0 = 300 \text{ K}$, and the difference $T_{\text{sh}} - T_0$ is expressed in degrees Centigrade.

Similarly, for VT in the form of Eqn (9.11) we get

$$T_{\text{sh}} - T_0 = \left\{ (\gamma - 1) \sum_n \frac{n}{2R} \left[3(\gamma - 1) - \sum_n n \right] \right\} \times \left[\frac{(P_{\text{sh}} V_{\text{sh}} - P_0 V_0)(6 + \sum_n n)}{\sum_n n} - (P_{\text{sh}} V_0 - V_{\text{sh}} P_0) \right]. \quad (9.23)$$

10. Algebraic method for calculating the correlation functions

In this section we shall briefly present the main aspects of the direct algebraic method for calculating the correlation functions in quantum statistical physics [52]. They are as follows.

1. We assume that for the system under consideration it is possible to construct a basis set of operators $\{\hat{A}_j\}$, which usually is *incomplete* but *closed* (not operator-wise) with respect to commutation with the Hamiltonian of the system:

$$[\hat{A}_j, H]_- = \sum_{j'=1}^n K_{jj'} \hat{A}_{j'}, \quad j = 1, 2, 3, \dots, n. \quad (10.1)$$

All operators in the set are generally of *different* orders. If all operators are of the same order, then the initial problem becomes completely *linearized*, so its solution will be exact, and the operator basis will be complete.

2. ‘Forced’ closure for the selected incomplete set of operators is accomplished by adjusting the values of coefficients $K_{nj'}$ in the expansion (10.1), using the yardstick of Jacobi’s operator identity which has to be satisfied exactly. For a two-operator basis, Jacobi’s identity is

$$[\hat{A}_1, [\hat{A}_2, H]_-]_- - [\hat{A}_2, [\hat{A}_1, H]_-]_- - [[\hat{A}_1, \hat{A}_2]_-, H]_- = 0. \quad (10.2)$$

Substituting here the expansions of the corresponding commutators

$$[\hat{A}_1, H]_- = K_{11} \hat{A}_1 + K_{12} \hat{A}_2$$

and

$$[\hat{A}_2, H]_- = K_{21} \hat{A}_1 + K_{22} \hat{A}_2$$

and the value of the cross-commutator $[\hat{A}_1, \hat{A}_2]_-$, we can find the required values of $K_{2j'}$. In this way, the entire inexactitude of the solution of the initial problem resides here in the K

matrix, and only in the elements $K_{nj'}$, since it is only the expansion of one last (n th) commutator that is not exact. The expansions of all other commutators are exact by dint of the procedure of their construction.

3. Basis $\{\hat{A}_j\}$ is constructed in such a way that any correlation function (CF) of the system should contain at least one of these operators. This requirement, together with the cyclic invariance of the trace of the product of operators (note that CF is such trace), and the *exact* formula of ‘undressing’

$$\hat{A}_j[\beta] = \sum_{j'=1}^n [\exp(-\beta K)]_{jj'} \hat{A}_{j'} \quad (10.3)$$

of the ‘dressed’ basis operator

$$\hat{A}_j[\beta] \equiv \exp(\beta H) \hat{A}_j \exp(-\beta H)$$

allows us immediately to find the closed (since n is finite) system of n algebraic equations with respect to the sought CF:

$$\langle \hat{B} \hat{A}_j \rangle = \langle \hat{A}_j[\beta] \hat{B} \rangle = \sum_{j'=1}^n [\exp(-\beta K)]_{jj'} \langle \hat{A}_{j'} \hat{B} \rangle,$$

$$j = 1, 2, 3, \dots, n,$$

$$\langle \dots \rangle \equiv \frac{\text{tr}[\exp(-\beta H) \dots]}{\text{tr}[\exp(-\beta H)]}. \quad (10.4)$$

If a CF includes several basis operators, it can be used for expressing the same number of independent equations.

Proof of Eqn (10.3). Let Eqn (10.1) hold. Then, using the rule of multiplication of matrices (see Ref. [64], p. 313)

$$(B^p)_{jj'} = \sum_{1,2,\dots,p-1} (B_{j1} B_{12} B_{23} \dots B_{p-1j}), \quad (10.5)$$

for the operator of p th order we get

$$[[\dots [\hat{A}_j, H]_-, H]_-, \dots]_-, H]_- = \sum_{j'} (K^p)_{jj'} \hat{A}_{j'}. \quad (10.6)$$

Now we substitute operators of type (10.6) into the *exact* series [65]

$$\hat{A}_j[\beta] = \hat{A}_j - \beta [\hat{A}_j, H]_- + \frac{\beta^2}{2!} [[\hat{A}_j, H]_-, H]_- - \dots \quad (10.7)$$

which immediately contracts into the exponent of the matrix argument:

$$\begin{aligned} \hat{A}_j[\beta] &= \sum_{j'} \left[\delta_{jj'} - \beta K_{jj'} + \frac{\beta^2}{2!} (K^2)_{jj'} - \dots \right] \hat{A}_{j'} \\ &= \sum_{j'} \left(1 - \beta K + \frac{\beta^2}{2!} K^2 - \dots \right)_{jj'} \hat{A}_{j'} \\ &= \sum_{j'} [\exp(-\beta K)]_{jj'} \hat{A}_{j'} \equiv \sum_{j'} F_{jj'}(\beta, K) \hat{A}_{j'}. \end{aligned} \quad (10.8)$$

4. Formula (10.4) — the main expression of the method of ‘dressing – undressing’ — features time-independent CF, which are conventional statistical means characterizing the equilibrium states of the system (when the Hamiltonian does not show an explicit dependence on time). The time dependence of CF does not require any considerable mod-

Obviously, the nonzero contributions only come from schemes 6, 7, 9, 11, 13, 14 and 15 from Eqn (A.4). So, for the initial quadruple sum we get the *exact* decomposition into nonzero sums of different order, namely: double (two), triple (four), and one completely primed quadruple:

$$\frac{1}{2} \sum_{1234} \langle 43|12 \rangle \hat{b}_4^+ \hat{b}_3^+ \hat{b}_1 \hat{b}_2 = 6 + 7 + 9 + 11 + 13 + 14 + 15. \quad (\text{A.6})$$

These terms correspond to analytical expressions

$$\begin{aligned} 6 &\equiv \frac{1}{2} \sum_{12} \langle 21|12 \rangle \hat{b}_2^+ \hat{b}_1^+ \hat{b}_1 \hat{b}_2 = \frac{1}{2} \sum_{12} \langle 21|12 \rangle \hat{n}_1 (\hat{n}_2 - \delta_{12}), \\ 7 &\equiv \frac{1}{2} \sum_{12} \langle 12|12 \rangle \hat{b}_1^+ \hat{b}_2^+ \hat{b}_1 \hat{b}_2 = \frac{1}{2} \sum_{12} \langle 12|12 \rangle \hat{n}_1 (\delta_{12} - \hat{n}_2), \\ 9 &\equiv \frac{1}{2} \sum_{124} \langle 41|12 \rangle \hat{b}_4^+ \hat{b}_1^+ \hat{b}_1 \hat{b}_2 = \frac{1}{2} \sum_{124} \langle 41|12 \rangle \hat{b}_4^+ \hat{b}_2 (\hat{n}_1 - \delta_{12}), \\ 11 &\equiv \frac{1}{2} \sum_{123} \langle 23|12 \rangle \hat{b}_2^+ \hat{b}_3^+ \hat{b}_1 \hat{b}_2 = \frac{1}{2} \sum_{123} \langle 23|12 \rangle \hat{b}_3^+ \hat{b}_1 (\hat{n}_2 - \delta_{12}), \\ 13 &\equiv \frac{1}{2} \sum_{123} \langle 13|12 \rangle \hat{b}_1^+ \hat{b}_3^+ \hat{b}_1 \hat{b}_2 = \frac{1}{2} \sum_{123} \langle 13|12 \rangle \hat{b}_3^+ \hat{b}_2 (\delta_{12} - \hat{n}_1), \\ 14 &\equiv \frac{1}{2} \sum_{124} \langle 42|12 \rangle \hat{b}_4^+ \hat{b}_2^+ \hat{b}_1 \hat{b}_2 = \frac{1}{2} \sum_{124} \langle 42|12 \rangle \hat{b}_4^+ \hat{b}_1 (\delta_{12} - \hat{n}_2), \\ 15 &\equiv \frac{1}{2} \sum_{1234}' \langle 43|12 \rangle \hat{b}_4^+ \hat{b}_3^+ \hat{b}_1 \hat{b}_2. \end{aligned}$$

In the last sum there are no coinciding indices: it is a completely primed sum. Now it is easy to see (taking advantage of the symmetry $\langle ij|ji \rangle = \langle ji|ij \rangle$ of the two-particle potential, and redefining the summation indices), that the second term on the right in Eqn (5.2) comes from the sum 6 + 7, the third term comes from the sum 9 + 11 + 13 + 14, and the last one from scheme 15, which will be dropped since it gives no contribution.

3. For numerical calculations of the EOS it may be useful (because of their intrinsic thermodynamic self-consistency) to recall the differential relations that follow from the fact that the differentials of various functions of state of the system are total differentials. The most important of these relations is the thermodynamic identity

$$T \left(\frac{\partial P}{\partial T} \right)_V = \left(\frac{\partial E}{\partial V} \right)_T + P, \quad (\text{A.7})$$

which states the relationship between the thermal $P = P(V, T)$ and caloric $E = E(V, T)$ equations of state of matter, and expresses the total condition

$$\left[\frac{\partial}{\partial V} \left(\frac{\partial F}{\partial T} \right) \right]_T = \left[\frac{\partial}{\partial T} \left(\frac{\partial F}{\partial V} \right) \right]_V \rightarrow \left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V \quad (\text{A.8})$$

for the differential

$$dF(V, T) = -S dT - P dV \quad (\text{A.9})$$

of free energy of the system. The isothermic derivative of the entropy of the system with respect to its volume is specified

with the aid of the differential

$$dS(V, E) = \frac{1}{T} dE + \frac{P}{T} dV, \quad (\text{A.10})$$

where we have yet to substitute the general explicit expression for $dE(V, T)$. Then Eqn (A.8) assumes its final form (A.7). From relation (A.9) we may express two more conditions of totality by rewriting it in terms of the differentials dT and dV :

$$dT = -\frac{P}{S} dV - \frac{1}{S} dF \rightarrow \left(\frac{\partial P}{\partial F} \frac{1}{S} \right)_V = \left(\frac{\partial 1}{\partial V} \frac{1}{S} \right)_F, \quad (\text{A.11})$$

$$dV = -\frac{1}{P} dF - \frac{S}{P} dT \rightarrow \left(\frac{\partial P}{\partial T} \frac{1}{S} \right)_F = \left(\frac{\partial S}{\partial F} \frac{1}{P} \right)_T, \quad (\text{A.12})$$

since both T and V also are functions of state of the system. Of course, out of the three conditions (A.8), (A.11), (A.12) one should use only that one which is best suited for a particular calculation, while the other two will be automatically satisfied. An entirely similar situation takes place for the Gibbs potential and entropy:

$$d\Phi(P, T) = -S dT + V dP, \quad (\text{A.13})$$

$$dS(P, H) = \frac{1}{T} dH - \frac{V}{T} dP, \quad (\text{A.14})$$

for which the main condition of totality

$$T \left(\frac{\partial V}{\partial T} \right)_P = V - \left(\frac{\partial H}{\partial P} \right)_T, \quad (\text{A.15})$$

is similar to Eqn (A.7). If, as already noted in Section 9, we use the representation $H(P, T) \equiv H_c(P) + H_{th}(P, T)$, we get

$$dH_c(P) = V_c(P) dP, \quad dH_{th}(P, T) = T dS + V_{th}(P, T) dP, \quad (\text{A.16})$$

$$T \left(\frac{\partial V_{th}}{\partial T} \right)_P = V_{th} - \left(\frac{\partial H_{th}}{\partial P} \right)_T. \quad (\text{A.16a})$$

Here the last expression is quite similar to Eqn (9.7a).

It will also be worthwhile to recall that the subscripts at thermodynamic partial derivatives stand to indicate explicitly the second independent variable, because the thermodynamic functions are thermodynamic potentials (of which one is sufficient for calculating all thermodynamic properties of the system) only when expressed in certain independent variables that are referred to as proper variables. For the internal energy E such are V, S ; for the free energy F — V, T , for the thermal function (enthalpy) H — P, S , for the Gibbs potential Φ — P, T . If a thermodynamic function is expressed in variables other than the proper variables [for example, $E(V, T)$ in place of $E(V, S)$], this will be not sufficient for the calculation of all thermodynamic properties of the system. Differentials of the functions of state of the system, however, will remain total differentials regardless of the selection of independent variables.

Another very important consequence of the totality of differentials of the functions of state relates to systems with two degrees of freedom. This relation follows from the differential of function of two independent variables, $z = z(x, y)$:

$$dz = \left(\frac{\partial z}{\partial x} \right)_y dx + \left(\frac{\partial z}{\partial y} \right)_x dy, \quad (\text{A.17})$$

where dx and dy are independent and entirely arbitrary increments. If we fix one of the independent variables in equality (A.17), it turns into a trivial identity like $dA = dA$. If, however, we fix the function $z(x, y)$ itself, then (A.17) becomes an *equation* in dx and dy :

$$0 = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy. \quad (\text{A.18})$$

To satisfy this equation, we now have to vary the values of dx and dy , which have become interdependent quantities, and their ratio can no longer be regarded as a partial derivative (at $z = \text{const}$) of one variable with respect to another: $dx/dy \equiv (\partial x/\partial y)_z$ or $dy/dx \equiv (\partial y/\partial x)_z$, although in Eqn (A.17) these ratios are zero because these variables do not depend on one another. Indeed, from Eqn (A.17) we get

$$\left(\frac{dz}{dx}\right)_y = \left(\frac{\partial z}{\partial x}\right)_y \cdot 1 + \left(\frac{\partial z}{\partial y}\right)_x \frac{dy}{dx} \rightarrow \frac{dy}{dx} = 0$$

and, similarly, $dx/dy = 0$. Thus, Eqn (A.18) can actually be rewritten as

$$\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x = -1. \quad (\text{A.19})$$

The thermodynamic functions — for example, $E = E(V, T)$, $F = F(V, T)$, $H = H(P, T)$, $\Phi = \Phi(P, T)$, $P = P(V, T)$ — for any simple thermodynamic system (that is, system with two degrees of freedom) must satisfy the relation (A.19).

Any EOS must also satisfy the condition of stability of equilibrium state of the system (the criterion of stability of equilibrium)

$$\left(\frac{\partial P_{\text{cr}}}{\partial x_{\text{cr}}}\right)_T \geq 0, \quad (\text{A.20})$$

where the equals sign corresponds to indifferent equilibrium (when the state of equilibrium is not affected by a change). Here P_{cr} is the thermodynamic potential, and x_{cr} is the corresponding thermodynamic coordinate. In particular, when $P_{\text{cr}} \equiv -P$ and $x_{\text{cr}} \equiv V$, then

$$\left(\frac{\partial P}{\partial V}\right)_T \leq 0. \quad (\text{A.20a})$$

4. Finally, by way of quick reference, we give a summary of the main results for a perfect gas — the touchstone of thermodynamics and statistical physics.

The thermal EOS for PG is [73–75]

$$P_{\text{th}}\Omega = \frac{m}{\mu} RT = \nu RT, \quad (\text{A.21})$$

where m is the mass of gas, Ω is its volume, μ is the molar mass of gas (which is numerically equal to molecular mass and is usually denoted by the same letter μ , as opposed to the molar mass, however, the molecular mass is dimensionless); $\nu = m/\mu$ is the number of mols, R is the universal gas constant. Sometimes it is convenient to express the EOS in terms of the number of gas particles N :

$$P_{\text{th}}\Omega = \frac{m}{\mu} N_A k_B T = N k_B T \rightarrow P_{\text{th}} = \frac{N}{\Omega} k_B T, \quad (\text{A.22})$$

because

$$N = N_A \nu = \frac{m}{\mu} N_A$$

($\Omega_{\text{mol}} = \Omega/\nu$, $N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$ is the Avogadro number, $k_B = R/N_A = 1.38 \times 10^{-23} \text{ J K}^{-1}$). In the physics literature, the EOS (like other relations) is usually written for unit mass (one gram in the physical system of units) of gas:

$$P_{\text{th}}V = \frac{RT}{\mu}, \quad P_{\text{th}}(V, T) = \frac{\rho RT}{\mu}, \quad (\text{A.23})$$

where $V = 1/\rho$, μV is the molar volume of the gas, $\rho/\rho_0 = \sigma$ is the degree of compression.

The internal energy of PG obviously depends only on its temperature:

$$E_{\text{th}}(T) = \frac{RT}{\gamma - 1} \mu, \\ \gamma = \frac{C_P}{C_V} = \frac{i + 2}{i} > 1 \rightarrow P_{\text{th}} = (\gamma - 1)\rho E_{\text{th}}, \quad (\text{A.24})$$

where i is the number of degrees of freedom of individual molecule of PG. Here the expression for E_{th} is the caloric EOS for PG, and the expression for P_{th} is the VT for PG. A perfect gas is the one and only thermodynamic system for which the virial theorem involves only its total internal energy. For all other systems the virial theorem involves separately the kinetic part of the total internal energy — that is, VT for PG is $f(E, P, V) = 0$, and for all other systems $f(E, E_{\text{kin}}, P, V) = 0$. This is because PG only has kinetic energy, and no potential energy.

Another curious property of PG is that its limiting compression caused by one shock wave (SW) can only take on *discrete* values. Indeed, since for PG we have $\gamma \equiv (C_P/C_V) = (i + 2)/i$, and i only assumes integral values $i = 0, 1, 2, \dots, \infty$, the value of γ can only be $2/0, 3/1, 4/2, 5/3, 6/4, \dots, 1$. This leads to a kind of ‘quantization’ of the limiting compression caused by one shock wave:

$$\rho_{\text{lim}} \equiv \left(\frac{\gamma + 1}{\gamma - 1}\right) \rho_0 = (1 + i)\rho_0 = \rho_0, 2\rho_0, 3\rho_0, \dots$$

We also reproduce here the diagrams of the basic processes for PG: isotherms (T), isentropes (S), and shock adiabats (SA). They are plotted in analytical (independent variable V or ρ , Fig. 3a) and in natural (independent variable P , Fig. 3b) coordinates.

In connection with these graphs [see, for example, the plot of function $P = P(\sigma)$] it will be interesting to consider the model case of shock compression of classical PG occurring initially at zero temperature $T = 0$. In this case, since $E_0 = P_0 = 0$, the equation of the shock adiabat for an arbitrary body [61, 62] [see Eqn (9.21)] assumes a very simple form for PG:

$$2E_{\text{th}} = (V_0 - V)P_{\text{th}} \rightarrow \frac{2VP_{\text{th}}}{\gamma - 1} = (V_0 - V)P_{\text{th}} \\ \rightarrow \frac{2V}{\gamma - 1} = (V_0 - V) \rightarrow \frac{\gamma + 1}{\gamma - 1} \equiv \varkappa = \frac{\rho}{\rho_0} \equiv \sigma, \quad (\text{A.25})$$

because P_{th} drops out from this relation since $P_{\text{th}} \neq 0$. Thus, the line $\sigma = \varkappa$ in this situation is the SA of PG at $T_0 = 0$. The temperature of gas on this line is $T_{\text{sh}} = P_{\text{sh}}/(A\kappa\rho_0)$, where

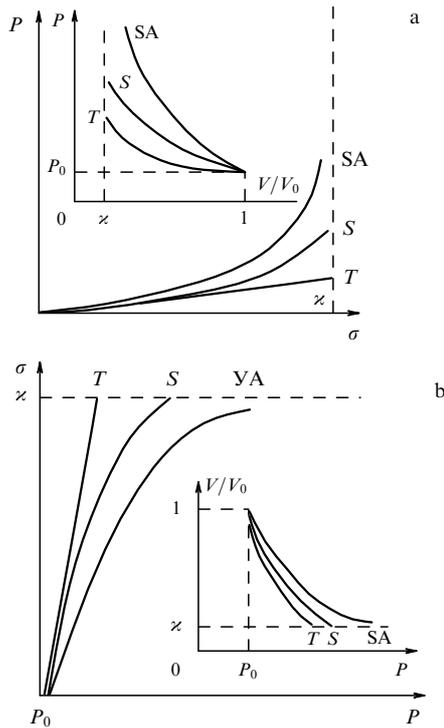


Figure 3.

$A \equiv R/\mu$ is the gas constant per unit mass of the gas. It is interesting to note that with such initial conditions a shock wave of arbitrary intensity (that is, any value of P_{sh}) causes extreme compression of the gas (because P_{sh} drops out from the equation for SA), so that as $T_0 \rightarrow 0$ the lines $T, S = \text{const}$ [see curve $P = P(\sigma)$] tend to align with the straight line $P(\sigma) = 0$, and the SA of the gas tends to align with the line $\sigma = \kappa$. The relation (A.25) is known as the thermodynamic SA. The kinematic SA for PG [59]

$$D^2 - D \frac{(\gamma + 1)u}{2} = \gamma P_0 V_0 \quad (\text{A.26})$$

under these conditions (that is, at $E_0 = P_0 = 0$) becomes a linear function of u :

$$D(u) = \frac{(\gamma + 1)u}{2}. \quad (\text{A.27})$$

Here D is the velocity of propagation of SW in unperturbed matter, u is the velocity of entrainment of matter downstream of the shock wave. Incidentally, this analytical result for PG apparently explains the linear dependence $D(u) = ku + b$ for solids (where we can always set $P_0 = 0$), discovered in the experiments on impact compression of solids. This dependence holds well for many solids away from the neighborhood of phase transitions. If, however, the impact compression is associated with a phase transition (for example, restructuring of the electron spectrum), then $D(u)$ becomes nonlinear in the neighborhood of PT: the points of phase transitions corresponding to slow compression become intervals of phase transitions in the case of impact compression (see the examples in the book [62] and in the reviews by L V Al'tshuler and colleagues [76, 77].

5. Acronyms: APW — attached plane waves; ASW — attached spherical waves; CCR — Corringi–Cohn–Rosstocker; CF — correlation function; EOS — equation of state; FBZ — first Brillouin zone; FODM — first-order

density matrix; HF — Hartree–Fock (approximation); IE — isoenergetic (line); IES — isoenergetic surface; PG — perfect gas; PT — phase transitions; SA — shock adiabat; SW — shock wave; TDF — theory of density functional; TF — Thomas–Fermi (model); VT — virial theorem; WSC — Wigner–Seitz cell.

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From reminiscences of A D Sakharov about N A Dmitriev

The youngest was Kolya (Nikolaĭ Aleksandrovich) Dmitriev, immensely talented, in those days he effortlessly produced one brilliant paper after another, marked with his mathematical genius. Zel'dovich used to say:

— Kolya is the only one among us who is blessed by God's gift. You might think he is a shy and quiet boy. But in fact we tremble before him like before the Judge of all men.

Kolya's giftedness transpired very early, he was a prodigy child. Supported by Kolmogorov, since the age of 15 he attended the University, passed all examinations in mathematics; as soon as he graduated from school he started working under Kolmogorov on the theory of probabilities. Kolmogorov viewed his results as very promising, and Kolya always came up to expectations. These, however, were separate episodes, while early in Kolya's career his 'beautiful' works formed a certain system. Shop became a factory. The call of duty compelled Kolya to churn out results, although by nature he was a master jeweler rather than a pieceworker. Zel'dovich tried to lure him into 'big physics', but nothing came out of it — Kolya was not one of those who can sit on two chairs. In later years he did much more than most others in the mathematical sector, but all the time there is a bitter feeling that in a different province he could have done something entirely different, something exceptional. Kolya was always interested in universal issues — philosophical, social, political. His attitude towards these issues reflected his absolute intellectual honesty, sharp paradoxical wit. Kolya was one of the few who did not exchange their medal of Stalin Prize laureate for the State Prize medal. He was keen on historical truth (like the Polish people who refused to rename the Stalin Palace in Warsaw). By his convictions and adamant stand Kolya is a nonconformist; he equally rejects the official ideology and my position. He is the only person from our facility who came to me openly after the publication of 'Contemplation on progress', and later 'Of state and world' (when I lived on Chkalov street) to borrow the books and discuss them. He thought I was completely wrong, but argued to the point⁶.

⁶ Sakharov A D *Atom* (1) 38 (1998) (founded by Russian Federal Nuclear Center — All-Russian Scientific Research Institute of Experimental Physics).