REVIEWS OF TOPICAL PROBLEMS

Thermodynamic fluctuations within the Gibbs and Einstein approaches

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Abstract. A comparative analysis of the descriptions of fluctuations in statistical mechanics (the Gibbs approach) and in statistical thermodynamics (the Einstein approach) is given. On this basis solutions are obtained for the Gibbs and Einstein problems that arise in pressure fluctuation calculations for a spatially limited equilibrium (or slightly nonequilibrium) macroscopic system. A modern formulation of the Gibbs approach which allows one to calculate equilibrium pressure fluctuations without making any additional assumptions is presented; to this end the generalized Bogolyubov-Zubarev and Hellmann - Feynman theorems are proved for the classical and quantum descriptions of a macrosystem. A statistical version of the Einstein approach is developed which shows a fundamental difference in pressure fluctuation results obtained within the context of two approaches. Both the 'genetic' relation between the Gibbs and Einstein approaches and the conceptual distinction between their physical grounds are demonstrated.

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Received 17 July 2000, revised 27 October 2000 Uspekhi Fizicheskikh Nauk **170** (12) 1265–1296 (2000) Translated by A S Dobroslavskiĭ; edited by A Radzig To illustrate the results, which are valid for any thermodynamic system, an ideal nondegenerate gas of microparticles is considered, both classically and quantum mechanically. Based on the results obtained, the correspondence between the microand macroscopic descriptions is considered and the prospects of statistical thermodynamics are discussed.

1. Introduction

The development of mesoscopic-level physics and applications of it (especially in the field of nanotechnologies) is associated with the increasing interest in studying more and more chaotic (including low-dimensional) systems (see, for example, Ref. [1]). Fluctuations of physical quantities are very important in such systems even at or near thermal equilibrium.

It would be reasonable to assume that the importance of the physics of fluctuations will only grow with time. From the theoretical standpoint, however, the situation with the description of fluctuations cannot yet be regarded as adequate.

Even leaving alone the yet unsolved problem of the linkage between quantum dynamic and thermodynamic fluctuations, one has to admit that any consistent description of proper thermodynamic fluctuations of physical quantities, characterizing the macroscopic system at or near thermal equilibrium, is currently not available.

1.1 Two approaches to the description of thermodynamic fluctuations

It is commonly held that thermodynamic fluctuations can be described on the basis of two distinct approaches: *statistical mechanics* or the Gibbs approach [2], and *statistical thermo-dynamics* or Einstein's approach [3] (the latter is sometimes loosely referred to as the quasi-thermodynamic theory of fluctuations). Despite the abundance of monographs and textbooks on statistical physics (see, for example, Refs [6, 7, 11, 13–32]), it is hard to find a comparative analysis of these two approaches. At the same time, the physical results of these two approaches tally far from always. For example, the two approaches give the same results for the dispersions of the extensive thermodynamic quantities, but different results for the dispersions of the intensive observables.

A careful analysis reveals that such disagreement arises neither by accident nor by mistake. As a matter of fact, it is a natural consequence of the conceptual distinction between the two approaches, even though both the approaches are statistical in nature. First of all, as opposed to Einstein's approach, the 'ensemble' ideology of the Gibbs approach excludes situations when in the state of thermal equilibrium between macroscopic system and thermostat, two thermodynamically conjugate macroscopic parameters may fluctuate simultaneously (for example, energy and temperature, volume and pressure, etc.)¹. Another important distinction is that the fluctuations themselves occur in an entirely different 'spaces of events': in the microscopic phase space according to Gibbs, and in the space of thermodynamic macroparameters according to Einstein.

In addition, the approaches of Gibbs and Einstein differ considerably in the treatment of the essential concept of thermal equilibrium or the zero principle of thermodynamics (this was apparently first noted by Planck [6]). Unlike the Gibbs approach, the approach of Einstein does not require the exact coincidence of the thermodynamic parameters descriptive of the macrosystem and thermostat. According to Einstein's approach, these parameters fluctuate in the macrosystem but not in the thermostat, so that the agreement between respective means is sufficient.

The distinction between the approaches of Gibbs and Einstein becomes even more vivid if we recall that the conventional methods of finding the statistical distribution functions descriptive of observed approaches are essentially different: the dynamic method is used in the Gibbs approach, and the thermodynamic method in Einstein's approach.

In view of the above, it seems worthwhile to discuss this range of problems, paying special attention to the conceptual distinctions between the approaches of Gibbs and Einstein, as well as to the 'genetic' linkage between these approaches. We shall also discuss the applicability of these approaches to the description of *actual stochastic* macroscopic systems in states close to thermal equilibrium.

In this review we have selected pressure fluctuations (PFs) as the typical study object for analyzing the similarities and differences of the approaches of Gibbs and Einstein. Such a choice is justified by the fact that it is the pressure (by contrast to, for example, the temperature or chemical potential) that has a straightforward and clear-cut physical meaning, and has an obvious mechanical 'prototype'. On top of that (see Section 1.2), the study of PFs is of interest on its own.

1.2 Problems of Gibbs and Einstein with regard to pressure fluctuations

According to the general principles of the statistical description of equilibrium macrosystems, the absolute *pressure dispersion* is defined as follows:

$$\overline{(\Delta P)^2} \equiv \overline{(P - \overline{P})^2} = \overline{P^2} - \overline{P}^2, \qquad (1.1)$$

where the over-bar denotes averaging over the distribution function used in the approaches of Gibbs and Einstein (where necessary, we shall specify this operation with superscripts G and E, respectively).

The two approaches differ in the physical meaning of pressure P even before the operation of averaging: in the Gibbs approach the pressure is generally a *dynamic* quantity, whereas in the Einstein approach it is a *thermodynamic* quantity. In addition, the averaging itself is not the same in the two approaches (for more details see Section 4).

There still is no consensus in the scientific literature (see Section 1.3) as to the method of calculating the pressure dispersion (1.1) even for an ideal gas of microparticles under the classical description in nondegenerate conditions. The results available in the Gibbs approach are rather inconsistent, and do not agree with the results obtained in the framework of Einstein's approach.

The calculation of PFs for macrosystems is a nontrivial task indeed; it splits into two problems which are naturally referred to as the *Gibbs problem* and the *Einstein problem*.

According to the Gibbs approach, the pressure dispersion (1.1) is defined by the following expression (see its development in Section 2.4)

$$\overline{\left(\Delta P\right)^2}^{\rm G} = \frac{1}{\beta} \left(\chi_T^{(P)} + \overline{\Psi} \right). \tag{1.2}$$

The right-hand side of Eqn (1.2), along with the conventional thermodynamic means — the isothermal compressibility $\chi_T^{(P)}$, and the pressure \overline{P} , i.e.

$$\chi_T^{(P)} \equiv \left[\frac{\partial \overline{P}}{\partial V}\right]_T = \frac{1}{\beta} \frac{\partial^2 \Phi(\beta, V)}{\partial V^2}, \quad \overline{P} = \frac{1}{\beta} \frac{\partial \Phi(\beta, V)}{\partial V}, \quad (1.3)$$

involves the so-called nonthermodynamic mean

$$\overline{\Psi} = -\frac{\overline{\partial P}}{\partial V} = \frac{\overline{\partial^2 \mathcal{H}_V}}{\partial V^2}, \qquad (1.4)$$

which, unlike the quantities (1.3), is not expressible in terms of the Massieu–Planck function $\Phi(\beta, V)$ and its derivatives. Obviously, thermodynamic stability of the macroscopic system is ensured by the inequalities

$$\chi_T^{(P)} < 0, \quad \overline{\Psi} > 0, \quad \overline{\Psi} > \left| \chi_T^{(P)} \right|.$$
 (1.5)

Expressions (1.3) are supplemented by the conventional definitions

$$\Phi(\beta, V) = \ln \mathcal{Z}(\beta, V), \quad \mathcal{Z}(\beta, V) = \int d\Gamma \exp\left[-\beta \mathcal{H}_{V}(\Gamma)\right],$$
(1.6)

where $\mathcal{Z}(\beta, V)$ is the statistical integral, $\mathcal{H}_V(\Gamma)$ is the Hamilton function, Γ is the set of arguments that define the phase space of the macrosystem in the classical case, the

¹ In this connection see, for example, the discussion in Refs [4, 5].

quantities $\beta = 1/k_BT$ and V have the meaning of the inverse temperature (thermodynamic parameter) and volume (mechanical external parameter). Expression (1.2) also holds for the quantum case, when $\mathcal{Z}(\beta, V)$ is the partition function, and $\hat{\mathcal{H}}_V$ is the Hamiltonian of the macrosystem.

The Gibbs problem for PFs is whether (and if so, how) it is possible to calculate the nonthermodynamic mean (1.4), while remaining within the framework of the Gibbs approach and without any additional assumptions.

The Einstein problem for PFs consists in that within Einstein's approach for the pressure dispersion (1.1), as demonstrated by Landau and Lifshitz [7], the following expression results:

$$\overline{\left(\Delta P\right)^2}^{\rm E} = -\frac{1}{\beta} \chi_S^{(P)} \,, \tag{1.7}$$

which is considerably different from Eqn (1.2) both in structure and in numerical value (this was apparently first noted by Münster [8]. Unlike relation (1.2), expression (1.7) only contains the thermodynamic mean — the adiabatic compressibility

$$\chi_{S}^{(P)} \equiv \left[\frac{\partial \overline{P}}{\partial V}\right]_{S} = \gamma \left[\frac{\partial \overline{P}}{\partial V}\right]_{T}, \qquad \chi_{S}^{(P)} < 0, \qquad (1.8)$$

where $\gamma = C_P/C_V > 1$ is the Poisson coefficient. It turns out that in all cases one has

$$\overline{\left(\Delta P\right)^2}^{\rm E} > \overline{\left(\Delta P\right)^2}^{\rm G} \,. \tag{1.9}$$

It must be noted that the problems of Gibbs and Einstein for PFs are encountered even for the simplest macroscopic system — an ideal gas (which we are going to use solely in our concrete calculations). The existing situation with the solution of these problems is far from being satisfactory (see Section 1.3). The aim of this paper is to give a consistent analysis of the Gibbs and Einstein problems and to propose constructive ways for their solution. The main difficulties, as will become clear from the discussion that follows, are associated not only with the computational hurdles but also with the conceptual basics of both approaches, and the feasibility of establishing links between them.

The main portion of the review that follows this introductory Section 1 is structured as follows. In Section 2 we give a brief listing of the main elements of the Gibbs approach, including the linkage between the dynamic and thermodynamic quantities (Sections 2.1 and 2.3), and present the combined Gibbs lemma for the correlation functions of physical quantity fluctuations (Section 2.4). Special attention is paid to the accurate definition (Section 2.2) of pressure P and compressibility Ψ as *quasi-dynamic* quantities (by analogy with the quasi-means in the sense of Bogolyubov [9]). In this case, the role of the external field that removes the spatial degeneracy of the macrosystem state is played by the singular potential of walls of the 'box' that encloses the system. Observe that the explicit form of this potential is not used anywhere (its 'projective' property is sufficient).

In Section 3 we introduce and explicitly construct the dynamic equations of state (DEOS) which relate the pressure and the compressibility to the Hamilton function or the Hamiltonian of the macrosystem (in the classical and quantum cases, respectively). With this purpose we generalize the theorems of Bogolyubov–Zubarev [10, 11] and Hellmann–Feynman [12, 13] (Sections 3.1 and 3.2). Statis-

tical averaging of DEOS (Section 3.3) leads to thermodynamic equations of state (TDEOS), which allows us to solve the Gibbs problem.

In Section 4 we present the Einstein approach and establish its 'genetic' linkage with the Gibbs approach (under the assumption of independence of the set of intensive parameters). The main element of this linkage is revealed by the 'stochastization' of the conjugate thermodynamic parameters upon transition 'from Gibbs to Einstein' (Section 4.2).

In Section 5 we extend the results of Section 4 to the case of the dependent intensive macroparameters that define the initial Gibbs ensemble. In Section 5.1 we obtain the 'working' expressions for the correlation functions and dispersions of the extensive macroparameters (which are the same for the approaches of Gibbs and Einstein), and for the correlation functions and dispersions of the intensive macroparameters in Einstein's approach.

Building on these results, in Section 5.2 we give a solution of Einstein's problem for PFs in the case of an ideal gas, and analyze the physical background of the disagreement between the results for PFs in the approaches under consideration. With this purpose we carry out the original calculation of PFs by statistical method using only the TDEOS of the macrosystem. In Section 5.3 we compare these results with those obtained in Ref. [7] by the traditional thermodynamic method of calculation of PFs, and also find the corrections to PFs that arise upon transition from the purely classical description for $T \ge T_0$ to the calculation that takes into account the lowest quantum (exchange) corrections for $T \ge T_0$, where T_0 is the temperature of degeneration of an ideal gas.

In the concluding Section 6 we discuss the general implications of the Gibbs and Einstein approaches as applied to the description of quasi-equilibrium states in stochastic macrosystems. This discussion is especially relevant in the context of the lively debate concerned with the relationship between statistical mechanics and statistical thermodynamics.

In the Appendix (Section 7) the reader will find the proof of the generalized Bogolyubov–Zubarev theorem, and the derivation of classical DEOS.

1.3 Brief review of the literature

The general problem of fluctuations of physical quantities in equilibrium and quasi-equilibrium states of macroscopic systems is discussed in practically all known treatises on statistical physics (see, for example, Refs [6-8, 11, 14-32]). However, the character of treating this problem as a whole (and the treatment of PFs, in particular) is much different.

Some of the above references [6, 11, 14, 16-22] treat the approaches of Gibbs and Einstein, while Refs [7, 15] only deal with Einstein's approach. In Refs [6, 11, 15, 20], however, PFs are not discussed at all, and in Refs [7, 14, 16-19, 21, 22] they are only worked out according to Einstein, and only by the thermodynamic calculating method.

So it is clear that none of the problems formulated in Section 1.2 can be found in the references cited above.

In some other sources [8, 23-32], the fluctuations of physical quantities are only considered within the framework of the Gibbs approach, and in Refs [23, 24, 26-29] PFs are not calculated at all, whereas in Refs [8, 25, 30-32] the Gibbs problem is formulated but, in our opinion, does not receive an adequate treatment. As far as the Einstein problem is concerned, to the best of our knowledge it is only formulated in Ref. [8], without any attempt at a solution.

Let us discuss in some detail the ways proposed for solving the Gibbs problem in the original papers [32-34], which actually served as basis for the treatments given in books [8, 31]. The formidability of a straightforward solution of the Gibbs problem within the framework of the Gibbs approach itself compelled the authors of Refs [32-34] (and some other researchers as well) to resort to various additional assumptions and technical tricks. Moreover, in Ref. [28] it is maintained that PFs can only be calculated with the methods of the theory of random processes, and in Ref. [35] the very existence of equilibrium pressure fluctuations is questioned.

As it is, the authors of Refs [32-34] proposed departing from the ensemble approach of Gibbs, and returning to the purely mechanical treatment of Bernoulli — the treatment based on the straightforward consideration of collisions between particles of the ideal gas and the walls of the container (which, for the sake of simplicity, is a cubic box). Then, according to Refs [32, 33], the particular form of the potential of interaction between particles and the walls of the container becomes important ² (which is different in Refs [32] and [33]). However, the use of model potentials in place of the exact singular potential of the idealized walls of the box leads (as the parameters characterizing the 'steepness' of the walls tend to infinity) to positive but divergent ³ expressions for the compressibility $\overline{\Psi}$, and to some other anomalies. Naturally, such results cannot be regarded as satisfactory.

In Refs [33, 34] it was proposed to vary the volume by moving the wall of the container with a finite velocity, and comparing it with the rate of changing the microstates of the particles, which effectively amounts to going beyond the scope of equilibrium thermodynamics. In this manner, keeping within the limits of applicability of Ehrenfest's adiabatic invariants, the authors of Refs [33, 34] gave a validation of the equality $\overline{\Psi} = -\chi_S^{(P)} = -\gamma\chi_T^{(P)}$, which, as will be shown below, holds at least for an ideal gas and gives in this case the solution of the Gibbs problem. In Refs [33, 34], however, this equality is derived outside the framework of the Gibbs approach.

Later in Ref. [8] — also with an additional tool (the Gibbs identity that links the mean values for the canonical and microcanonical ensembles) — an expression for the PFs in an ideal gas was obtained that only holds in the case of the classical description.

From this brief review of the available literature it is clear that the situation with the Gibbs and Einstein problems for PFs is quite perplexing, which originally stimulated this paper. In our opinion, we have succeeded in giving sufficiently convincing solutions of both problems.

2. Main elements of the Gibbs approach for the canonical ensemble

2.1 Dynamic quantities and dynamic equations of state

The Hamiltonian function and generalized forces. As is known (see, for example, Refs [2, 7, 11]), the dynamic or the purely

mechanical description of adiabatically isolated macrosystem of N interacting microparticles (where $N \ge 1$) is based on a certain set of *dynamic* quantities $X_V(\Gamma; \{a\})$, where $\{a\} = (a_1, \ldots, a_k, \ldots)$ is the set of mechanical parameters (as a rule, external force fields), V is the volume occupied by the system in the configuration space, and all the parameters $\{a\}$ and V are given by the environment of the macrosystem⁴.

If the macrosystem is not adiabatically isolated but is in thermal equilibrium with the thermostat, the external parameters are supplemented by the thermodynamic parameters (for example, the temperature *T*, the chemical potential μ , etc.). By definition, however, the dynamic quantities cannot depend on these (such a dependence is only exhibited by their mean values \overline{X} ; see Section 2.2).

The dynamic nature of quantities $X_V(\Gamma; \{a\})$ consists in that they are all defined in the phase space of the macrosystem $\{\Gamma\}$ (or part of it), which is the set of all possible (or admissible) values of 2fN dynamic variables — the canonically conjugate momenta $\{p\}$ and coordinates $\{q\}$. Here and further f = 1, 2, 3 is the number of translational degrees of freedom of each particle⁵, which coincides with the dimensionality of the configuration space; the dimensions of the coordinate $\{q\}$ and momentum $\{p\}$ parts of the phase space $\{\Gamma\}$ are the same, and equal to fN. If there are no restrictions imposed on the macrosystem, then all f momenta and coordinates ($\alpha = 1, \ldots, f$) of each of the N particles $(i = 1, \ldots, N)$ assume all possible values

$$-\infty < p_i^{(\alpha)} < \infty, \quad -\infty < q_i^{(\alpha)} < \infty.$$
 (2.1)

The quantum analogs of dynamic quantities $X_V(\Gamma; \{a\})$ are the operators $\hat{X}_V(\{a\})$ which act in the space of wave functions of the macrosystem in question.

The main dynamic quantity that, according to Gibbs [2], determines the thermodynamic properties of a macrosystem at the state of thermal equilibrium, is the *energy* of the system ⁶. In the classical description, the energy of the system is defined by the Hamiltonian function $\mathcal{H}(\Gamma; \{a\})$, and in the quantum description⁷ by the Hamiltonian $\hat{\mathcal{H}}(\hat{q}, \hat{p}, \{a\})$.

If the system is free (all $\{a\} = 0$) and unlimited $(V \to \infty)$, then its Hamiltonian function $\mathcal{H}^{(0)}(\Gamma) \equiv \mathcal{H}^{(0)}(q, p)$ depends only on the dynamic variables p and q of the system itself. If there are mechanical external parameters or generalized coordinates $\{a\}$, then it is expedient to introduce the canonically conjugate generalized forces $\{A\} = (A_1, \dots, A_k, \dots)$:

$$A_k(\Gamma; \{a\}) \equiv -\frac{\partial \mathcal{H}(\Gamma; \{a\})}{\partial a_k} .$$
(2.2)

As a rule, the homogeneous static force fields which enter the Hamiltonian function $\mathcal{H}(\Gamma; \{a\})$ as a *linear* combination

² It was Maxwell who, when deriving the equilibrium statistical distribution for an ideal gas, demonstrated that the form of this distribution (and hence the form of all mean values) cannot depend on the particulars of the contact interaction of particles with walls of the container, or particles with one another.

³ Observe that Gibbs [2] admitted the feasibility of 'very large' (but apparently finite) values of the dynamic compressibility Ψ (and accordingly $\overline{\Psi} > |\chi|$).

⁴ In future we shall always assume that N = const, which implies impermeability of the walls bounding the volume *V*.

⁵ For the sake of simplicity we assume that the microparticles do not possess any internal degrees of freedom. As long as the translational motion and the internal motions are independent, however, the inclusion of internal degrees of freedom does not affect the results obtained here.

⁶ Without compromising the generality, we may assume that all other integrals of motion of this system (the total momentum and the total angular momentum) are zero.

⁷ Further on we shall write all formulas in the classical version, while the transition to the quantum description will be specially stipulated (see, for example, Section 3.2).

assume the role of the external parameters $\{a\}$. Then, according to Eqn (2.2), we have

$$\mathcal{H}(\Gamma; \{a\}) = \mathcal{H}(\Gamma) - \sum_{k} a_k A_k(\Gamma) , \qquad (2.3)$$

with the generalized forces $A_k(\Gamma)^8$ themselves no longer depending on $\{a\}$, so that for any k and l the equality is valid:

$$\frac{\partial A_k(\Gamma)}{\partial a_l} = -\frac{\partial^2 \mathcal{H}(\Gamma; \{a\})}{\partial a_l \partial a_k} = 0.$$
(2.4)

Observe that because of Eqns (2.4) and (2.3) the definition (2.2) is purely formal, since it yields an identity when combined with Eqn (2.3) [equation (2.2) is only convenient for calculating the mean values of generalized forces \overline{A}_k ; see Section 2.3]. As a matter of fact, for the quantities $A_k(\Gamma)$ (at least for their values per unit volume) in the case of a completely free macrosystem there is a definition independent of $\mathcal{H}^{(0)}(\Gamma)$ in terms of dynamic variables p, q and certain physical characteristics of particles (charge, mass, electrical and magnetic dipole moments, etc.). Needless to say the external field a may affect \overline{A}_k , so that $\overline{A}_k(a) \neq \overline{A}_k(0)$. But generally $A_k(\Gamma; 0) \neq 0$.

Volume and pressure. A thermodynamically equilibrium macrosystem may be free (all $\{a\} = 0$) but it must necessarily be enclosed — that is, it must have a finite volume *V* and must be separated from the environment (thermostat) by 'walls' of some kind. For the sake of simplicity in the subsequent discussion we assume that the volume is a cubic box with the edge *L*; it is also considered that the walls conduct heat but are impenetrable for the microparticles. This means that not the entire coordinate part $\{q\}$ of the phase space is accessible to the system: it splits into two regions, namely, $\{q\} = \{q\}^{(I)} \oplus \{q\}^{(II)}$, where $\{q\}^{(I)}$ is the spatial domain inside the box, and $\{q\}^{(II)}$ is the region outside the box including its walls. Accordingly, for the allowable values of *p* and *q* for any *i* and α , in place of Eqn (2.1) we have

$$\begin{aligned} & -\infty < p_i^{(\alpha)} < \infty \,, \quad -\frac{L}{2} < q_i^{(\alpha)} < \frac{L}{2} \,, \\ & \{q_i^{(\alpha)}\} \in \{q\}^{(1)}, \quad L = V^{1/f}, \quad f = 1, 2, 3, \quad 0 < V < \infty. \end{aligned}$$

Depending on the physical conditions of the contact between macrosystem and thermostat, different types of impermeable walls are possible (with N = const); we shall consider two possible situations: isobaric (constant pressure, P = const), and isochoric (constant volume, V = const).

(1) In the *isobaric* case, the *pressure* P is set in the capacity of the external intensive generalized coordinate, and the walls (at least one wall of the six) are assumed to be *movable*, so that the size of the region $\{q\}^{(I)}$ may vary. Then the extensive generalized force (the dynamic quantity) is the *volume*

$$V(\Gamma; a, P) = -\frac{\partial \mathcal{H}(\Gamma; a, P)}{\partial P} .$$
(2.6)

The meaning of the isobaric situation is that at the state of thermal equilibrium the mean value \overline{V} adjusts so as to balance

the pressure in the system and the externally applied pressure P^9 , so that $\overline{V} = \overline{V}(P)$. Then in the framework of the Gibbs approach the volume V can fluctuate, while the pressure P cannot, and the Gibbs problem for pressure fluctuations does not arise at all (we shall only consider such a situation in Section 5.1 in connection with the transition from the Gibbs to the Einstein approach).

It is obvious that the quantity (2.6) is completely similar to the quantity (2.2) in the following respect. Just like the quantities $A_k(\Gamma)$ can be computed independently of definition (2.2) in the case a = 0, the quantity $V(\Gamma)$ can be calculated at P = 0. Consequently, the quantity $V(\Gamma)$ does not depend on P (unlike, of course, the mean value \overline{V}). Therefore, at $P \neq 0$ the Hamiltonian function becomes

$$\mathcal{H}(\Gamma; a, P) = \mathcal{H}(\Gamma; a) - PV(\Gamma), \qquad (2.7)$$

where according to definition (2.5)

$$V(\Gamma) = \int \prod_{\alpha=1}^{f} dq_{i}^{(\alpha)}, \quad q_{i}^{(\alpha)} \in \{q\}^{(1)}, \quad (2.8)$$

and

$$\frac{\partial V(\Gamma)}{\partial P} = -\frac{\partial^2 \mathcal{H}(\Gamma; P)}{\partial P^2} = 0.$$

(2) The statement and solution of the Gibbs problem for PFs is based below on the *isochoric* situation, which assumes that the walls are fixed and absolutely rigid. Then the external extensive generalized coordinate is the volume V^{10} , which is conjugated with the intensive generalized force represented by the pressure $P_V(\Gamma; a)$, with

$$P_{V}(\Gamma; a) = -\frac{\partial \mathcal{H}_{V}(\Gamma; a)}{\partial V} .$$
(2.9)

This definition agrees well with the conventional *mechanical* definition of pressure as the normal force acting upon unit area of the walls, used by Daniel Bernoulli in the 18th century for relating the pressure to the kinetic energy of particles of an ideal gas.

According to Eqn (2.9), the pressure produced by the macrosystem is a dynamic quantity, and in the framework of the Gibbs approach exhibits both the mean value \overline{P} and the fluctuations (see Sections 2.3 and 2.4). Despite the outward similarity between definitions (2.9) and (2.6) and (2.2), there is also an important distinction. It is impossible in principle to define the internal pressure for an unbounded system $(V \to \infty)$ described by the Hamiltonian function $\mathcal{H}^{(0)}(\Gamma)$, since

$$P^{(0)}(\Gamma) = -\frac{\partial \mathcal{H}^{(0)}(\Gamma)}{\partial V} \equiv 0$$
(2.10)

(in other words, 'no walls — no pressure'). This means that the pressure $P_V(\Gamma)$ has no independent definition other than (2.9), unlike $A_k(\Gamma)$ and $V(\Gamma)$.

In addition, as will be shown below, unlike $\{a\}$ and *P* the parameter *V* enters the Hamiltonian function $\mathcal{H}_V(\Gamma)$ in an essentially nonlinear manner. Because of this, in addition to

⁸ For the sake of simplicity, further we shall confine ourselves to one pair of conjugate quantities a and A. In most of the concrete calculations of pressure and its fluctuations we shall assume that the macrosystem is free — that is, a = 0.

⁹ It is easy to see the complete analogy with the isothermal situation, T = const, when the mean energy of the system $\overline{\mathcal{H}}$ settles at the value $\overline{\mathcal{H}}(T)$ determined by the externally set temperature *T*.

¹⁰ Hereinafter we shall denote the dependence on volume V for dynamic quantities with the appropriate subscript.

the dynamic quantity — pressure (2.9), there is another nonzero quantity 11 — the *dynamic compressibility*

$$\Psi_V(\Gamma; a) = -\frac{\partial P_V(\Gamma; a)}{\partial V} = \frac{\partial^2 \mathcal{H}_V(\Gamma; a)}{\partial V^2} \neq 0, \qquad (2.11)$$

as well as, generally speaking, higher derivatives of \mathcal{H}_V with respect to V. The difference in properties of quantities (2.4) and (2.11) is important in calculating fluctuations of quantities A_k and P (see Section 2.4).

Equations of state. Just as in the Gibbs approach the practice is to distinguish between the dynamic quantities A(p,q) pertaining to the microscopic description of the system and the thermodynamic (mean) quantities \overline{A} pertaining to the macroscopic description, we hold it necessary also to distinguish between the respective equations of state. If, for example, for some particular macroscopic system it is possible to calculate independently the right-hand sides of Eqns (2.9) and (2.11), then relations (2.9) and (2.11) acquire the sense of the *dynamic equations of state* (DEOS-I and DEOS-II, respectively). The averaging of these equations according to Gibbs in the state of thermal equilibrium leads to equations of state in the conventional sense — the thermodynamic equations of state (TDEOS-I and TDEOS-II, respectively).

The first of these equations (TDEOS-I), which relates the mean pressure \overline{P} to the volume V and temperature T, is referred to as the *thermal* equation of state; it is equivalent to the classical *Clausius virial theorem* (for more details see Section 3.1). As far as the second equation (TDEOS-II) is concerned, it is not found in the scientific literature known to us. At the same time, as shown in Section 2.3, it is TDEOS-II together with the isothermal compressibility $\chi_T^{(P)}$ that determines the PFs and allows in principle the solution of the Gibbs problem for a system of a sufficiently general form. The consistent derivation of the two dynamic equations of state, which are used in turn for expressing the two TDEOS, constitutes the burden of Section 3.

2.2 Pressure and compressibility as quasi-dynamic quantities

In connection with the definition of pressure, there is the issue of the adequate introduction of the volume V into the Hamiltonian function $\mathcal{H}_V(\Gamma, a)$, so as to give meaning to definition (2.9) [definition (2.7) is obviously not suitable, because it leads to an identity]. The difficulty consists in the possible dual interpretation of the designated finite volume V.

(1) On the one hand, the parameter V reflects a rather simple and purely kinematic constraint in the form (2.8). It is clear that in this case the parameter V does not enter explicitly into the Hamiltonian function $\mathcal{H}(\Gamma)$ [or the Hamiltonian $\hat{\mathcal{H}}(\hat{q}, \hat{p})$] but is rather introduced 'by hand' at the stage of averaging in the classical description, or as an additional boundary condition in the quantum description. As a result, definitions (2.9) and (2.11) do not work, and equations DEOS-I and DEOS-II simply have no physical meaning. As a rule, this circumstance is ignored in the scientific literature but does not create any complications only because the DEOS-II for compressibility $\Psi_V(\Gamma, a)$ is commonly left unconsidered at all, and neither is the equation TDEOS-II for the nonthermodynamic mean $\overline{\Psi}_V$ which determines the PFs.

¹¹ Not to be confused with the conventional thermodynamic compressibility $\chi = \partial \overline{P} / \partial V$, where \overline{P} is the mean pressure.

As far as DEOS-I for the pressure $P_V(\Gamma, a)$ is concerned, this equation is usually interesting not by itself but only for expressing TDEOS-I for the mean pressure \overline{P}_V . It is obvious that TDEOS-I has meaning only because the quantity \overline{P}_V according to Eqn (1.3) is a thermodynamic mean. (Indeed, in the course of averaging according to Eqn (2.9), the derivative with respect to V is 'switched over' from the Hamiltonian function \mathcal{H} to the functions Φ and \mathcal{Z} .) Then, in the statistical integral (and consequently in the Massieu – Planck function), the dependence on the parameter V appears in the integration with respect to $d\Gamma$ in Eqn (1.6) in accord with the kinematic constraints of the form (2.5) [for more details see Section 2.3, formulas (2.26) and (2.27)]. Obviously, for nonthermodynamic means (including $\overline{\Psi}_V$) such a procedure is not possible by definition, which mandates finding a different way of expressing the initial DEOS.

(2) On the other hand, one may assume that the parameter V shows evidence of a *dynamic* (force) quantity, because the walls of the box bounce all the incident particles back into the box, thus ensuring its impermeability in both the classical and quantum descriptions. Then the dynamic nature of the volume V can be taken into account by adding to the Hamiltonian function of the unbounded macroscopic system, $\mathcal{H}^{(0)}(\Gamma; a)$, the external singular repulsive potential ¹²

$$U_{V}(q) = \begin{cases} 0, & \text{for all } \{q_{i}^{(\alpha)}\} \in \{q\}^{(\mathrm{I})}, \\ \infty, & \text{for any } \{q_{i}^{(\alpha)}\} \in \{q\}^{(\mathrm{II})}, \end{cases}$$
(2.12)

where $\{q_i^{(\alpha)}\}$ is the set of all *f* coordinates $(\alpha = 1, ..., f)$ of all *N* particles (i = 1, ..., N) in the macrosystem; the definitions of regions $\{q\}^{(I)}$ and $\{q\}^{(II)}$ were given in front of Eqn (2.5).

Observe that such a dynamic equivalent of kinematic constraints is used in a number of other physical problems. For example, the inclusion of quantum indistinguishability of microparticles and the symmetry properties of the complete wave function even in the ideal gas model gives rise to an additional 'exchange' term in the Hamiltonian $\hat{\mathcal{H}}$ (see, for example, Refs [7, 21, 26]). This term describes the effective repulsion (attraction) for a Fermi or Bose gas, respectively, which is entirely absent in a Maxwell – Boltzmann gas. Such a correction is necessary for the degenerate regime (which is not considered in this paper); however, the contribution from quantum exchange corrections to TDEOS and PFs in the nondegenerate regime (in the lowest order in powers of T_0/T , where T_0 is the degeneracy temperature of the gas) is accounted for in Section 5.4.

In this way, the total Hamiltonian function of the bounded macrosystem must be written as

$$\mathcal{H}_{V}^{(\varepsilon)}(\Gamma; a) = \mathcal{H}^{(0)}(\Gamma; a) + \varepsilon U_{V}(q) \,. \tag{2.13}$$

Similarly, for the Hamiltonian we get

$$\widehat{\mathcal{H}}_{V}^{(\varepsilon)}(\hat{q},\hat{p};a) = \widehat{\mathcal{H}}^{(0)}(\hat{q},\hat{p};a) + \varepsilon U_{V}(\hat{q}), \qquad (2.14)$$

where the formal parameter ε may take on any positive values. As will be shown in Section 3, it is the dynamic treatment of the volume V as the external parameter that best matches the Gibbs approach and allows, in particular, the solution of the Gibbs problem for PFs. In practice, however, it is quite

¹² A similar potential (the 'hard-core' model type) is usually also used in the description of mutual collisions between absolutely rigid particles of finite size.

difficult to implement definitions (2.9) and (2.11) with the Hamiltonian function (2.13) owing to the singular delta-shaped potential (2.12).

In our opinion, the most natural way out of this complication consists in following the ideas of the Bogolyubov method of quasi-averages [9]. This means that in place of the conventional dynamic quantities (2.9) and (2.11) in the framework of the classical description of a macrosystem (Section 3.1) it is expedient to consider the *quasi-dynamic* quantities — the pressure

$$\widetilde{P}_{V}^{(0)}(\Gamma) = \lim_{\varepsilon \to +0} P_{V}^{(\varepsilon)}(\Gamma) = \lim_{\varepsilon \to +0} \left(-\frac{\partial \mathcal{H}_{V}^{(\varepsilon)}(\Gamma)}{\partial V} \right), \quad (2.15)$$

and the compressibility

$$\widetilde{\Psi}_{V}^{(0)}(\Gamma) = \lim_{\epsilon \to +0} \left(-\frac{\partial P_{V}^{(\epsilon)}(\Gamma)}{\partial V} \right) = \lim_{\epsilon \to +0} \left(-\frac{\partial^{2} \mathcal{H}_{V}^{(\epsilon)}(\Gamma)}{\partial V^{2}} \right).$$
(2.16)

Then, generally speaking, unlike Eqn (2.11) we have

$${\widetilde \Psi}_V^{(0)}({\Gamma})
eq - rac{\Im {\widetilde P}_V^{(0)}({\Gamma})}{\Im V}\,,$$

so that DEOS-I and DEOS-II must be developed independently of one another. In the quantum description (Section 3.2), *quasi-operators* will be defined for these quantities in a similar fashion.

The meaning of definitions (2.15) and (2.16) is as follows. After the potential $U_V(q)$, like Schiller's moor ¹³, has done its job (raising a wall in the system), like the moor it has to depart — and the physical results must not be dependent on the form of $U_V(q)$ but must instead be completely determined by the form of $\mathcal{H}^0(\Gamma)$. In the method of quasi-averages [9], the role of 'the moor' is usually played by the external field proportional to ε , which removes the degeneracy of the system and ensures the nonzero mean value of the degenerate physical quantity in the limit of $\varepsilon \to 0$. In our case, such a procedure ought to be accomplished yet at the level of dynamic quantities — the pressure and the compressibility become nonzero when the potential $U_V(q)$ is applied to remove the degeneracy ¹⁴ of the macrosystem described by the initial Hamiltonian function $\mathcal{H}^{(0)}(\Gamma)$.

Calculation of the right-hand sides in Eqns (2.15) and (2.16) yields the explicit form of the classical DEOS-I and DEOS-II. This calculating method and the result obtained for a very general case comprise the content of the generalized *Bogolyubov*–*Zubarev theorem*, which is discussed in Section 3.1 (for a complete proof see Section 7). Similar calculations for quantum macrosystems and a derivation of corresponding quantum DEOS constitute the generalized *Hellmann*–*Feynman theorem*, discussed in Section 3.2. It is important that in all cases the quantities $\tilde{P}_V^{(0)}(\Gamma)$ and $\tilde{\Psi}_V^{(0)}(\Gamma)$ (or their quantum counterparts) are completely determined by the form of the initial Hamiltonian function $\mathcal{H}^{(0)}(\Gamma)$ alone (or the corresponding Hamiltonian).

¹³ "The moor has done his job, let the moor depart" — quote from Friedrich Schiller's play 'Fiesco's Conspiracy at Genoa' (Act 3, Scene 4) (1783) — *Transl. note.*

Notwithstanding some difference in the methods and details of computations, the classical and quantum descriptions share one important common property with respect to the inclusion of the singular potential $U_V(q)$ from Eqn (2.12). According to the general approach (see, for example, Ref. [39]), the operations of differentiation of singular functions (2.15) and (2.16) (and the quantum counterparts of these expressions) are conveniently expressed in terms of functionals of some kind or another. Then the potential (2.12) acts similarly to the *projection operator* onto the states with finite volume V in the corresponding space of states of the macrosystem.

Obviously, for the *states* in the classical description it is convenient to take the coordinate part $\{q\}$ of the phase space of the macrosystem, and in the quantum description the wave functions $|q\rangle$ in Schrödinger's *q*-representation. Accordingly, the statistical integral $\mathcal{Z}^{(\varepsilon)} = \int d\Gamma \exp[-\beta \mathcal{H}_V^{(\varepsilon)}(\Gamma)]$ is used for the *functionals* in the classical case, and the mean value of the Hamiltonian, $\langle q | \hat{\mathcal{H}}_V^{(\varepsilon)} | q \rangle$, in the quantum case. The projection in the classical case is onto the finite region $\{q\}^{(1)}$ of the phase subspace $\{q\}$ (the volume enclosed by the box), and in the quantum case onto the family of wave functions that satisfy the boundary condition $|q\rangle = 0$ on the inner surface of the box of volume V.

2.3 Mean values and thermodynamic equations of state

Statistical mechanics or the Gibbs approach [2] is based on the ergodic hypothesis which allows replacement of the time averages of the dynamic quantities by the statistical ensemble averages of the same quantities. It is these averages that are identified in the Gibbs approach with the observables at the state of thermal equilibrium. This means that in such a state every dynamic quantity $X_V(\Gamma; a)$ is a random variable in the phase space Γ (but, of course, a single-valued function of *a* and V parameters). It is important here that the Gibbs distribution function $\rho_V^{\rm G}(\Gamma; a)$ is the same for all quantities $X_V(\Gamma; a)$ and depends only on the form of the statistical ensemble for the system under consideration. The selection of the ensemble in its turn depends on the conditions of thermal equilibrium, defined by the set of thermodynamic and mechanical parameters¹⁵ which are determined by the environment.

In the event of isothermal and isochoric ensemble (canonical ensemble according to Gibbs), this set contains just one thermodynamic parameter $T \equiv 1/k_{\rm B}\beta = \text{const}$, and one mechanical parameter V = const. Then, according to Gibbs theorem [2], the function $\rho^{\rm G}$ takes the form

$$\rho_V^{\rm G}(\Gamma; a, \beta) = \exp\left[-\Phi(a, V, \beta) - \beta \mathcal{H}_V(\Gamma; a)\right].$$
(2.17)

The Massieu–Planck function Φ in Eqn (2.17) is found from the normalization condition imposed on ρ^{G} :

$$\rho_V^{\rm G}(\Gamma; a, \beta) \,\mathrm{d}\Gamma = 1\,. \tag{2.18}$$

Here and further the element of phase volume is

$$\mathrm{d}\Gamma = \frac{\mathrm{d}p \,\mathrm{d}q}{N! (2\pi\hbar)^f}, \quad \mathrm{d}p \,\mathrm{d}q \equiv \prod_{\alpha=1}^f \prod_{i=1}^N \,\mathrm{d}p_i^{(\alpha)} \,\mathrm{d}q_i^{(\alpha)} \,, \qquad (2.19)$$

¹⁵ Observe that in the formal limit $N \to \infty$, when the fluctuations of physical quantities describing the macrosystem are unimportant, all the ensembles become thermodynamically equivalent (see, for example, Refs [11, 25]).

¹⁴ This degeneracy is due to the spatial homogeneity and the invariance of the initial Hamiltonian function with respect to an arbitrary transformation of coordinates $\{q\}$ in the configuration space, including one into another mapping of the internal and external (with respect to volume *V*) regions $\{q\}^{(I)}$ and $\{q\}^{(II)}$, defined by condition (2.12).

and integration in Eqn (2.18) and subsequent expressions (2.21) for Z and (2.23) for the mean values is performed over the region of phase space $\{\Gamma\}$ accessible to the macrosystem. If there are no constraints, the integration in these expressions according to Eqn (2.1) is performed over all possible values of momenta and coordinates of all the particles.

In the quantum case, the integration over the phase space in Eqn (2.18) (and in other expressions involving this operation) is replaced by summation over all quantum states accessible to the system.

To facilitate the notation, we introduce the designation $\{x\} \equiv (a, V, \beta)$ for the set of all external parameters governing the Massieu–Planck function and some other quantities ¹⁶; then the quantity x will denote any of the parameters from the set $\{x\}$. Substituting function (2.17) into condition (2.18), we find

$$\exp\left[-\Phi\{x\}\right]\mathcal{Z}\{x\} = 1.$$
(2.20)

Here

$$\mathcal{Z}\{x\} \equiv \int \exp\left[-\beta \mathcal{H}_{V}(\Gamma;a)\right] \mathrm{d}\Gamma$$
(2.21)

is the classical *statistical integral* (by assumption, it has a finite value for all or at least for some of the values of parameters entering $\{x\}$).

From Eqn (2.20) it follows that

$$\Phi\{x\} = \ln \mathcal{Z}\{x\} = -\beta \mathcal{F}\{x\}, \qquad (2.22)$$

where $\mathcal{F}{x}$ is the thermodynamic potential (the Helmholtz free energy), commonly used in the calculations based on the canonical ensemble.

As will become clear from the discussion to follow (especially in Sections 4 and 5), the Massieu–Planck function $\Phi\{x\}$ in some respects is more convenient than $\mathcal{F}\{x\}$ by virtue of its 'generating' properties with respect to all variables in the set $\{x\}$ (in particular, with respect to the dimensionless inverse temperature β , the use of which is more natural than the use of the thermodynamic temperature T). Observe that the dependence on a and V of the functions \mathcal{Z}, Φ and \mathcal{F} is defined directly by the Hamiltonian function (2.13), whereas the dependence on β is introduced by the Gibbs canonical distribution function (2.17).

The mean value of the arbitrary dynamic quantity $X_V(\Gamma; a)$ in the Gibbs approach is defined as follows

$$\overline{X}\{x\} \equiv \int X_V(\Gamma; a) \,\rho^{\rm G}(\Gamma; \{x\}) \,\,\mathrm{d}\Gamma\,, \qquad (2.23)$$

where the common practice is to distinguish between *thermodynamic and nonthermodynamic* averages. The former include those mean values that can be expressed in terms of the function $\Phi\{x\}$ and its derivatives of any order with respect to any of its arguments entering $\{x\}$; all the rest are classified as nonthermodynamic mean values.

In this way, the computation of any mean values of the first type reduces to finding just one quantity $\mathcal{Z}{x}$. It is well known that this calculation is difficult by itself, and depends considerably on the form of the Hamiltonian function \mathcal{H} . The

calculation of the mean values of the second type, however, is an even more formidable task, which may be referred to as *the Gibbs problem in the broad sense*. No general formulas are available for its solution, and in every event one needs to know the explicit form of the quantity $X_V(\Gamma; a)$. Further we shall only be interested in the particular case of the Gibbs problem, related to the calculation of PFs when $X_V(\Gamma; a)$ coincides with $\Psi_V(\Gamma; a) = -\partial^2 \mathcal{H}_V(\Gamma; a)/\partial V^2$.

The thermodynamic averages in the context of the canonical Gibbs ensemble include first of all the mean values of the Hamiltonian function itself (the mean or internal energy) and the mean values of its derivatives — the generalized forces (2.2) and pressure (2.9). The equation for the mean value $\overline{\mathcal{H}}$ is usually referred to as the caloric TDEOS, and those for the mean values $\overline{\mathcal{A}}$ and $\overline{\mathcal{P}}$ as the thermal TDEOS.

The appropriate TDEOS can be developed by differentiating sequentially the normalization condition (2.18) with respect to each variable x from the set $\{x\}$. Then we get

$$\int d\Gamma \rho^{G}(\Gamma; \{x\}) = 1, \quad \int d\Gamma \, \frac{\partial \rho^{G}(\Gamma; \{x\})}{\partial x} = 0, \qquad (2.24)$$

where, according to Eqn (2.17), one finds

$$\frac{\partial \rho^{G}(\Gamma; \{x\})}{\partial x} = -\rho^{G}(\Gamma; \{x\}) \left\{ \frac{\partial \Phi\{x\}}{\partial x} - \mathcal{D}_{x}(\Gamma; \{x\}) \right\}.$$
(2.25)

Here we have introduced the generalized (in this case, a threecomponent) dynamic quantity

$$\mathcal{D}_{x}(\Gamma; \{x\}) \equiv -\frac{\partial}{\partial x} \left[\beta \mathcal{H}_{V}(\Gamma; a)\right], \ \{x\} \equiv \{a, V, \beta\}, \ (2.26)$$

which allows us to simplify and unify the expressions for both the mean values and the fluctuations and correlations.

Substituting expression (2.25) into the second equation in (2.24), and considering the first equation and definition (2.23), we find that

$$\frac{\partial \Phi\{x\}}{\partial x} - \overline{\mathcal{D}}_x = 0, \quad \overline{\mathcal{D}}_x \equiv \overline{\mathcal{D}}_x(\Gamma; \{x\}).$$
(2.27)

From Eqn (2.27) we see that all the mean values \overline{D}_x are, according to our definition, thermodynamic averages. Setting the variable x in the right-hand side of Eqn (2.26) equal sequentially to a, V and β , we get

$$\mathcal{D}_a = \beta A, \quad \mathcal{D}_V = \beta P, \quad \mathcal{D}_\beta = -\mathcal{H}.$$
 (2.28)

Having regard to the general expression (2.27) for the averages \overline{D}_x , we express the thermal TDEOS

$$\overline{\mathcal{D}}_a = \beta \overline{A} = \frac{\partial \Phi}{\partial a} , \quad \overline{A} = \frac{1}{\beta} \frac{\partial \Phi}{\partial a} , \qquad (2.29)$$

$$\overline{\mathcal{D}}_{V} = \beta \,\overline{P} = \frac{\partial \Phi}{\partial V} \,, \quad \overline{P} = \frac{1}{\beta} \,\frac{\partial \Phi}{\partial V} \,, \tag{2.30}$$

and the caloric TDEOS

$$\overline{\mathcal{D}}_{\beta} = -\overline{\mathcal{H}} = \frac{\partial \Phi}{\partial \beta} , \quad \overline{\mathcal{H}} = -\frac{\partial \Phi}{\partial \beta} . \tag{2.31}$$

Obviously, all the results obtained in this section for the classical case also hold their forms for the quantum case; then for the Massieu–Planck function one should use not its

¹⁶ Arguments of functions may be dropped as long as this does not lead to confusions.

classical form $\Phi_{\rm C}$ as defined by Eqn (2.22), but rather the quantum expression $\Phi_{\rm Q} = \ln Z_{\rm Q}$, where the partition function is given by

$$\mathcal{Z}_{Q}\{x\} = \operatorname{Sp}\exp\left[-\beta\widehat{\mathcal{H}}_{V}(a)\right].$$
(2.32)

2.4 Fluctuations and correlation functions

Along with its mean value (2.23), any random dynamic quantity $X_V(\Gamma; \{a\})$ is also characterized by its deviation from this mean value called *fluctuation*:

$$\Delta X(\Gamma; \{x\}) \equiv X_V(\Gamma; a) - \overline{X}\{x\}, \qquad (2.33)$$

and by virtue of the linearity of averaging operation in Eqn (2.23), we obviously have

$$\Delta X(\Gamma; \{x\}) \equiv 0. \tag{2.34}$$

Because of this, an adequate measure of fluctuations is only given by the $\{x\}$ -dependent bilinear *correlation functions* of the form

$$\overline{\Delta X \Delta Y} \equiv \int \Delta X(\Gamma; \{x\}) \, \Delta Y(\Gamma; \{x\}) \, \rho^{\rm G}(\Gamma; \{x\}) \, \mathrm{d}\Gamma \,, \, (2.35)$$

where $Y_V(\Gamma; a)$ in the general case is an arbitrary dynamic quantity. In particular, if Y = X, then the measure of fluctuations is the *autocorrelation function or the absolute variance*

$$\overline{(\Delta X)^2} \equiv \overline{(\Delta X(\Gamma; \{x\}))^2} = \overline{X_V^2(\Gamma; a)} - \overline{X}^2\{x\}.$$
(2.36)

Obviously, both the absolute variance (2.36) and the *relative* variance ξ_X^2 satisfy the condition of thermodynamic stability:

$$\overline{(\Delta X)^2} \ge 0, \quad \xi_X^2 \equiv \overline{(\Delta X)^2} / \overline{X}^2 \ge 0.$$
 (2.37)

Of particular interest is the case when Y in formula (2.35) is substituted by the generalized quantity \mathcal{D}_x from Eqn (2.26). In this case the *combined Gibbs lemma* holds, which according to Ref. [2] (see also Ref. [31]) can be obtained by differentiating the mean value (2.23) with respect to any variable x from the set $\{x\}$. Then we have

$$\frac{\partial \overline{X}}{\partial x} = \int d\Gamma \left\{ \frac{\partial X_V(\Gamma; a)}{\partial x} \rho^G(\Gamma; \{x\}) + X_V(\Gamma; a) \frac{\partial \rho^G(\Gamma; \{x\})}{\partial x} \right\}$$
$$= \frac{\overline{\partial X}}{\partial x} + \int d\Gamma \rho^G(\Gamma; \{x\}) X_V(\Gamma; a) \Delta \mathcal{D}_x(\Gamma; \{x\}). (2.38)$$

Here we have used the fact that, by virtue of relation (2.27) and definition (2.33), the derivative of the function ρ^{G} from Eqn (2.25) can be written in a more convenient form

$$\frac{\partial \rho^{\mathbf{G}}(\Gamma; \{x\})}{\partial x} = \rho^{\mathbf{G}}(\Gamma; \{x\}) \, \Delta \mathcal{D}_{x}(\Gamma; \{x\}) \,.$$

Taking into account definition (2.33) and the property (2.34) for ΔD_x , it is easy to find the final expression for the correlation function (2.35) with $Y = D_x$:

$$\overline{\Delta X \Delta \mathcal{D}_x} = \chi^{(X;x)} + \psi^{(X;x)}, \qquad (2.39)$$

where, by definition 17, one has

$$\chi^{(X;x)} \equiv \frac{\partial \overline{X}}{\partial x}, \quad \psi^{(X;x)} \equiv -\frac{\overline{\partial X}}{\partial x}, \quad (2.40)$$

and for any given X the quantities (2.40) have three components each.

The physical meaning of quantities χ and ψ is sufficiently clear. The quantities χ are the generalized thermodynamic susceptibilities that define the so-called *static* response, which is the change of the mean values \overline{X} under very slow variations of the external parameter x (field a, volume V, or temperature $T = 1/k_B\beta$). The values of ψ are the mean values of the 'dynamic' susceptibilities (or, as Gibbs called them, mechanical 'elasticities' [2]). It is obvious that in the general case for arbitrary X the quantities of both types are not thermodynamic averages — that is, they are not expressible in terms of the function Φ and its derivatives with respect to x.

If we confine our treatment to the analysis of correlation functions only for the three-component dynamic quantity \mathcal{D}_x , then in formula (2.39) we must set $\Delta X = \Delta \mathcal{D}_{x'}$. Then, setting in the general case $x' \neq x$, we find

$$\overline{\Delta \mathcal{D}_{x'} \Delta \mathcal{D}_{x}} = \chi^{(\mathcal{D}_{x'};x)} + \psi^{(\mathcal{D}_{x'};x)} .$$
(2.41)

It is obvious that the matrix of correlation functions (2.41) consists of nine components. Using definition (2.40) and considering expression (2.27) for $\overline{D}_{x'}$, we arrive at

$$\chi^{(\mathcal{D}_{x'};x)} = \frac{\partial \overline{\mathcal{D}}_{x'}}{\partial x} = \frac{\partial^2 \Phi}{\partial x \partial x'}, \qquad (2.42)$$

whence it follows that all nine quantities in the last formula are thermodynamic averages.

Accordingly, using definition (2.40) and considering expression (2.26) for $\mathcal{D}_{x'}$, we get

$$\psi^{(\mathcal{D}_{x'};x)} = -\frac{\overline{\partial \mathcal{D}_{x'}}}{\partial x} = \frac{\partial^2}{\partial x \partial x'} \left[\beta \mathcal{H}_V(\Gamma;a) \right].$$
(2.43)

It is easy to verify that out of nine quantities in relationship (2.43) five are zero, three are thermodynamic averages, and only one (at x = x' = V) which defines just the PFs is a nonthermodynamic average — that is, the subject of the Gibbs problem.

Indeed, let us consider in greater detail the 'diagonal' case x' = x in expression (2.4<u>1</u>), which corresponds to the calculation of the variance $(\Delta D_x)^2$, and set x equal sequentially to a, β , and V. At x = a, according to Eqns (2.43) and (2.28), we obtain

$$\psi^{(\mathcal{D}_a;a)} = -\frac{\overline{\partial \mathcal{D}_a}}{\partial a} = -\beta \frac{\overline{\partial \mathcal{A}}}{\partial a} = 0.$$
(2.44)

Here we have used the property (2.4) of linearity of the Hamiltonian function \mathcal{H} with respect to the external field *a*, so that for the variance of the generalized force we have

$$\overline{(\Delta A)^2} = \frac{1}{\beta} \frac{\partial \overline{A}}{\partial a} = \frac{1}{\beta^2} \frac{\partial^2 \Phi}{\partial a^2} .$$
(2.45)

¹⁷ When the derivative is taken with respect to any variable *x*, all other variables from the set $\{x\}$ are assumed fixed.

Similarly, with $x = \beta$, according to Eqns (2.43) and (2.28), we get

$$\psi^{(\mathcal{D}_{\beta};\beta)} = -\frac{\overline{\partial \mathcal{D}_{\beta}}}{\partial \beta} = \frac{\overline{\partial \mathcal{H}}}{\partial \beta} = 0.$$
(2.46)

Since the Hamiltonian function \mathcal{H} , like any other dynamic quantity, does not depend on β , for the energy variance we find

$$\overline{\left(\Delta\mathcal{H}\right)^2} = -\frac{\partial\overline{\mathcal{H}}}{\partial\beta} = \frac{1}{k_{\rm B}\beta^2} C_{V,a} = \frac{\partial^2\Phi}{\partial\beta^2}, \qquad (2.47)$$

where $C_{V,a} = \partial \overline{\mathcal{H}} / \partial T$ is the heat capacity at constant volume and fixed external field ¹⁸. Observe that in the cases (2.45) and (2.47) the condition of stability (2.37) is satisfied when the corresponding thermodynamic susceptibilities $\chi^{(\mathcal{D}_a;a)}$ and $\chi^{(\mathcal{D}_{\beta};\beta)}$ are positive.

The most complicated situation arises at x = V, since the quantity

$$\psi^{(\mathcal{D}_{V};V)} = -\frac{\overline{\partial}\overline{\mathcal{D}_{V}}}{\overline{\partial}V} = -\beta\frac{\overline{\partial}\overline{P}}{\overline{\partial}V} = \beta\frac{\overline{\partial}^{2}\overline{\mathcal{H}}}{\overline{\partial}V^{2}}$$
(2.48)

in the general case is nonzero owing to the property (2.11) of nonlinearity of \mathcal{H} with respect to V. Accordingly, the pressure dispersion in the Gibbs approach is written as

$$\overline{(\Delta P)^2}^{G} = \frac{1}{\beta} \left[\chi^{(P;V)} + \psi^{(P;V)} \right].$$
(2.49)

Here we have taken into account that

$$\chi^{(\mathcal{D}_{V};V)} = \beta \chi^{(P;V)}, \quad \psi^{(\mathcal{D}_{V};V)} = \beta \psi^{(P;V)}, \quad (2.50)$$

and

$$\chi^{(P;V)} \equiv \chi_T^{(P)} = \frac{\partial \overline{P}}{\partial V} = \frac{1}{\beta} \frac{\partial^2 \Phi}{\partial V^2}$$
(2.51)

is the conventional thermodynamic susceptibility (in this case, the isothermal compressibility), while

$$\psi^{(P;V)} = -\frac{\overline{\partial P}}{\partial V} = \frac{\partial^2 \mathcal{H}}{\partial V^2}$$
(2.52)

is the nonthermodynamic average of the 'dynamic elasticity'. Thus, the relations (2.49), (2.51) and (2.52) reconstruct the formula (1.2), i.e. one of the seminal formulas of this paper.

Comparing the expressions (2.45), (2.47) and (2.49), it is easy to verify that the pressure dispersion (2.49) is much different from the variances of generalized force (2.45) or energy (2.47). First of all, to ensure the thermodynamic stability of the macrosystem, the thermodynamic susceptibilities in the cases (2.45) and (2.47) are positive, whereas the quantity $\chi_T^{(P)}$ in formula (2.49) is always negative. Secondly, the expressions (2.45) and (2.47) do not contain the nonthermodynamic term, whereas in formula (2.49) this term is nonzero. What is more, in order to satisfy condition (2.37) in this case it is necessary that the quantity $\psi^{(P;V)} \equiv \overline{\Psi}$ be positive and greater (in absolute value) than $\chi^{(P;V)} \equiv \chi_T^{(P)}$, which is equivalent to condition (1.5).

3. Equilibrium pressure fluctuations in the Gibbs approach

As follows from the results of Section 2 [in particular, from expression (2.49)], calculation of equilibrium PFs requires knowing the quantities $\chi = \partial \overline{P}/\partial V$ and $\Psi = -\partial \overline{P}/\partial V$. Since, according to Eqns (2.30) and (2.51), the quantities \overline{P} and χ are thermodynamic averages, the problem reduces to finding the explicit form (with subsequent averaging) of DEOS-II, as defined by Eqn (2.16). Observe that the calculations using formulas (2.30) and (2.51) do not require knowing DEOS-I as defined by Eqn (2.15); however, the derivation of the latter is nevertheless of interest, especially for nonideal macrosystems.

For the particular case of an ideal gas it turns out that the quasi-dynamic quantity $\tilde{P}(\Gamma)$ (and, similarly, the compressibility $\tilde{\Psi}(\Gamma)$) is no longer independent at the dynamic level and is a linear function of the energy $\mathcal{H}(\Gamma)$ (which, as a matter of fact, has been known to D Bernoulli). This observation immediately brings us to a simple thermal TDEOS which is directly proportional to the caloric TDEOS [see Eqn (3.22)]. The circumstance that is especially interesting for us is that the problem of calculating pressure fluctuations reduces thereby to the calculation of energy fluctuations ¹⁹. The latter, according to formula (2.47), is much simpler because it does not involve nonthermodynamic averages.

Thus, in the case of an ideal gas the Gibbs problem has an additional solution apart from the direct one. Of course, both methods of calculating PFs, as will be shown below, lead to the same results. It is important that all the postulates formulated above equally apply (see Section 3.2) to both classical and quantum descriptions of an ideal gas.

In the more general case of a nonideal macrosystem, the DEOS for pressure and compressibility can also be developed for both classical and quantum descriptions, but the methods of their derivation differ essentially. The fact is that the boundary conditions stemming from the existence of walls and being of major interest for the problem considered have to be taken into account in a principally different manner. In the quantum or even quasi-classical descriptions, the microparticles — by virtue of their wave properties — 'feel' the *global* properties of the wall potential (2.12). This leads to the dependence of the eigenfunctions and eigenvalues of the Hamiltonian of the system on the volume V. Differentiating these with respect to V, one may then apply the Hellmann – Feynman theorem (Section 3.2) to obtain the quantum DEOS.

In the purely classical case, where the wave properties are completely ignored, the particles only 'feel' the *local* properties of the potential at the walls (2.12). In other words, the particles are only engaged in the contact interaction with the walls, and this interaction only shows itself in straightforward collisions ²⁰. In so doing, the boundary conditions and the dependence on V are only involved in the limits of integration for the statistical integral (2.21). The dependence on the volume V of the quasi-dynamic quantities can only be found in explicit form by applying the canonical scale transformation to variables of the phase space. Then one can apply the Bogolyubov–Zubarev theorem (Section 3.1) to developing

¹⁸ Hereinafter we consider the simplest case of a = 0, and explicitly indicate the remaining arguments V and T from the set $\{x\}$.

¹⁹ This result confirms Münster's hypothesis [8].

 $^{^{20}}$ Of course, within the statistical Gibbs approach, by contrast to the purely mechanical approach of Bernoulli, there is no need to consider explicitly the details of this interaction. Its role (like the role of collisions between the particles) reduces to the system thermalization — that is, to the establishment of an equilibrium distribution of the form (2.17).

the classical DEOS — that is, explicitly calculating the righthand sides in relations (2.15) and (2.16).

The applicability of the results obtained in this way is essentially different: in the classical case the range of applicability is much broader than in the quantum case. Indeed, the classical DEOS can be obtained for a macrosystem described by the arbitrary (including also nonadditive with respect to p and q) Hamiltonian function $\mathcal{H}(p,q)$ — its differentiability with respect to p and q will suffice for this purpose. A similar degree of generality in the quantum case would imply finding the energy spectrum for the macrosystem with an arbitrary Hamiltonian $\hat{\mathcal{H}}(\hat{p}, \hat{q})$, which in the general form is hardly feasible.

3.1 DEOS in the classical description.

Generalization of the Bogolyubov-Zubarev theorem

The derivation of DEOS-I for the pressure as a quasi-dynamic quantity (2.15) makes up the content of the *Bogolyubov*–*Zubarev theorem*, first applied in Ref. [10] and further developed in Ref. [11]. Building on the proof evolved in Refs [10, 11] (see Section 7), we proposed a generalization of this theorem — the development of DEOS-II for the compressibility as a quasi-dynamic quantity (2.16), not found in the scientific literature before. It should be observed that the literature also has no references to the explicit use of the idea of Bogolyubov's method of quasi-averages [9] in connection with the proof of the Bogolyubov–Zubarev theorem.

The Bogolyubov–Zubarev theorem and method are applied to the system of interacting microparticles described by the Hamiltonian function $\mathcal{H}^{(0)}(q,p)$ of a sufficiently general form [the superscript '0' has the meaning of $\varepsilon = 0$ in the context of formula (2.13)]. The main conclusion of the Bogolyubov–Zubarev theorem is that the limit (2.15) exists and is equal to

$$\widetilde{P}_{V}^{(0)}(\Gamma) \equiv \widetilde{P}_{V}^{(0)}(p,q) = -\frac{1}{fV} \left[\frac{\partial \mathcal{H}^{(0)}(p/\lambda,\lambda q)}{\partial \lambda} \Big|_{\lambda=1} \right]. \quad (3.1)$$

This expression represents DEOS-I for the system under consideration, whose explicit form depends on the form of the function $\mathcal{H}^{(0)}(p,q)$.

We used the same method to demonstrate (see paragraphs 3, 4 in Section 7) that the limit (2.16) also exists and is equal to

$$\begin{split} \widetilde{\Psi}_{V}^{(0)}(\Gamma) &\equiv \widetilde{\Psi}_{V}^{(0)}(p,q) \\ &= \frac{1}{V} \widetilde{P}_{V}^{(0)}(p,q) + \frac{1}{(fV)^{2}} \left[\frac{\partial \mathcal{H}^{(0)}(p/\lambda,\lambda q)}{\partial \lambda} \right|_{\lambda=1} \\ &+ \frac{\partial^{2} \mathcal{H}^{(0)}(p/\lambda,\lambda q)}{\partial \lambda^{2}} \Big|_{\lambda=1} \right]. \end{split}$$
(3.2)

This expression represents DEOS-II for the same system; its explicit form is also determined by the form of the Hamiltonian function $\mathcal{H}^{(0)}(p,q)$. It is important that the quantity (3.2) required for calculating the pressure fluctuations cannot be obtained directly from formula (3.1) by performing differentiation with respect to the volume *V*.

The proof of relationships (3.1) and (3.2) is based on the functionals

$$\mathcal{Z}_{V}^{(\varepsilon)} = \int \mathrm{d}\Gamma \exp\left[-\beta \mathcal{H}_{V}^{(\varepsilon)}(\Gamma)\right],\tag{3.3}$$

$$\mathcal{Z}^{(0)}(V) = \int_{\dots V \dots} d\Gamma \exp\left[-\beta \mathcal{H}^{(0)}(\Gamma)\right].$$
(3.4)

Expression (3.3) involves $\mathcal{H}_{V}^{(e)}(\Gamma)$ defined in Eqn (2.13), and the domain of integration (2.1) with respect to $d\Gamma$ has no constraints; hence formula (3.3) displays an improper integral and admits differentiation with respect to the parameter V. The integral (3.4) involves $\mathcal{H}^{(0)}(\Gamma)$ from Eqn (2.13), but its domain of integration {...V...} with respect to the coordinate part of { Γ } has restrictions of the form (2.5). Accordingly, the differentiation with respect to V in formula (3.4) reduces to the differentiation of the integral with respect to its upper limit.

The details of the derivation of relations (3.1) and (3.2) can be found in the Appendix (Section 7); here we only mark the main points of the procedure. First, we proceed from an almost evident equality

$$\lim_{\varepsilon \to +0} \mathcal{Z}_{V}^{(\varepsilon)} = \mathcal{Z}^{(0)}(V); \qquad (3.5)$$

it suffices to take into account that the integrand in formula (3.3) can be represented as

$$\exp\left[-\beta \mathcal{H}_{V}^{(\varepsilon)}(\Gamma)\right] = \exp\left[-\beta \mathcal{H}_{V}^{(0)}(\Gamma)\right] \Delta_{V}^{(\varepsilon)}(q) , \qquad (3.6)$$

where by definition

$$\Delta_{V}^{(\varepsilon)}(q) \equiv \exp\left[-\beta \varepsilon \, U_{V}(q)\right] = \\ = \begin{cases} 1, & \text{for all } \{q_{i}^{(\alpha)}\} \in \{q\}^{(\mathrm{I})}, \\ 0, & \text{for any } \{q_{i}^{(\alpha)}\} \in \{q\}^{(\mathrm{II})}. \end{cases}$$
(3.7)

Indeed, with due account for Eqn (2.12), the quantity (3.7) with arbitrary $\varepsilon > 0$ acts as the operator that 'projects' the entire configuration space $\{q\}$ onto the internal region $\{q\}^{(I)}$ of the box of volume *V*, and 'cuts off' its external region $\{q\}^{(II)}$ (the definitions of these regions were given before Eqn (2.5)).

Performing differentiation of Eqns (3.3) and (3.4) with respect to V, it is easy to verify that the equalities hold good (n = 1, 2):

$$\lim_{\varepsilon \to +0} \frac{\partial^n \mathcal{Z}_V^{(\varepsilon)}}{\partial V^n} = \frac{\partial^n \mathcal{Z}^{(0)}(V)}{\partial V^n} .$$
(3.8)

As demonstrated in Section 7, these equalities actually contain expressions (3.1) and (3.2) at n = 1, 2, respectively. Indeed, the left-hand sides of equalities (3.8) under the sign of integration $\int d\Gamma \exp[-\beta \mathcal{H}^{(0)}(\Gamma)]$... contain definitions of the quantities $\widetilde{P}_{V}^{(0)}(\Gamma)$ and $\widetilde{\Psi}_{V}^{(0)}(\Gamma)$ [the left-hand sides of relations (3.1) and (3.2)]. The right-hand sides of Eqn (3.8) lead correspondingly to the right-hand sides of Eqns (3.1) and (3.2).

The efficient method proposed in Refs [10, 11] for calculating the right-hand sides in formula (3.8) consists in the following. The canonical scale transformation is applied to the variables p and q (momenta and coordinates of the translational motion of particles) that does not alter the volume element of the phase space (2.19):

$$p \to p' = \lambda p, \quad q \to q' = \lambda^{-1} q, \quad d\Gamma' = d\Gamma,$$
 (3.9a)

with

$$\mathcal{H}^{(0)}(p,q) = \mathcal{H}^{(0)}(p'/\lambda,\lambda q').$$
(3.9b)

Here, the parameter λ may assume any nonzero real value. As a result, the differentiation of $\mathcal{Z}^{(0)}(V)$ from the integral (3.4)

with respect to the upper limit V is 'switched over' to the differentiation of $\mathcal{H}^{(0)}(p/\lambda, \lambda q)$ with respect to the parameter λ (see paragraphs 2, 4 in Section 7).

Observe once again that in the entire treatment of the quasi-dynamic quantities — the pressure and the compressibility — the wall potential $\varepsilon U_V(q)$ plays a necessary but auxiliary role, justifying the prefix 'quasi'. As a matter of fact, after completion of the action as the projection operator according to Eqn (3.7), and transition to the limit $\varepsilon \to +0$ in equalities (3.8), this potential is completely removed from subsequent calculations²¹. As a result, DEOS (3.1) and (3.2) are fully defined by the form of the Hamiltonian function $\mathcal{H}(p,q)$ of the original (unbounded) macrosystem.

For a nonideal macrosystem of a sufficiently general form, the Hamiltonian function $\mathcal{H}(p,q)$ can be represented as a sum of two terms: the kinetic energy $\mathcal{H}(p)$, and the potential energy $\mathcal{H}(q)$. As a rule, $\mathcal{H}(p)$ and $\mathcal{H}(q)$ are additive functions:

$$\mathcal{H}(p) = \sum_{i=1}^{N} \mathcal{H}(p_i), \quad \mathcal{H}(q) = \frac{1}{2} \sum_{i \neq j}^{N} \mathcal{H}(q_i, q_j), \quad (3.10)$$

that is, the kinetic energy appears as the sum of one-particle terms, and the potential energy is the sum of two-particle interactions.

In many physically essential cases the above two energies are *homogeneous functions* of their respective arguments with the exponents k and l, respectively, so that

$$\mathcal{H}(\lambda^{-1}p) = \lambda^{-k}\mathcal{H}(p), \quad \mathcal{H}(\lambda q) = \lambda^{l}\mathcal{H}(q).$$
(3.11)

In particular, if $\mathcal{H}(p)$ and $\mathcal{H}(q)$ are power functions, then the homogeneity indices *k* and *l* coincide with the corresponding power exponents²².

For a highly general case (3.11), DEOS-I and DEOS-II from (3.1) and (3.2) become

$$P_V(p,q) = \frac{1}{fV} \left[k \mathcal{H}(p) - l \mathcal{H}(q) \right], \qquad (3.12)$$

$$\Psi_{V}(p,q) = \frac{1}{V} P_{V}(p,q) + \frac{1}{(fV)^{2}} \left[k^{2} \mathcal{H}(p) + l^{2} \mathcal{H}(q) \right].$$
(3.13)

A useful observation is that the quantity $l\mathcal{H}(q)$ in Eqn (3.12) has the meaning of the *Clausius force virial*

$$-l\mathcal{H}(q) = q\mathcal{F}(q), \quad \mathcal{F}(q) \equiv -\frac{\partial\mathcal{H}(q)}{\partial q}.$$

Averaging Eqn (3.12) over the canonical ensemble, we come to TDEOS-I, which has the meaning of the classical *virial theorem*²³:

$$\overline{P}(V,T) = \frac{k}{fV} \overline{\mathcal{H}(p)} - \frac{l}{fV} \overline{\mathcal{H}(q)}.$$
(3.14)

²¹ To simplify the notation, we further drop the '~' sign and superscript '0' in the quantities (3.1) and (3.2), and also set $\mathcal{H}^{(0)}(p,q) \equiv \mathcal{H}(p,q)$.

 23 This theorem is usually established (see, e.g. Ref. [21]) by averaging the time-domain equations of motion for the dynamic variables — the momenta and coordinates of the particles in the system.

Averaging formula (3.13), we correspondingly get TDEOS-II:

$$\overline{\Psi}(V,T) = \frac{1}{V} \overline{P}(V,T) + \frac{1}{(fV)^2} \left[k^2 \overline{\mathcal{H}(p)} + l^2 \overline{\mathcal{H}(q)} \right], (3.15)$$

which gives a constructive solution of the Gibbs problem formulated in Section 1.2. This means that the nonthermodynamic quantity $\overline{\Psi}$ is expressed as a linear combination of the averages: the mean pressure \overline{P} (a thermodynamic quantity), and the mean energies — the mean kinetic energy $\overline{\mathcal{H}(p)}$ and the mean potential energy $\overline{\mathcal{H}(q)}$, separately. (Recall that it is only their sum, the total internal energy $\mathcal{H}(p,q)$, which is a thermodynamic average.)

Differentiating DEOS-I (3.14) with respect to the volume V (at T = const) and noting that $\partial \overline{\mathcal{H}(p)} / \partial V = 0$, for isothermal compressibility we find

$$\chi_T^{(P)} = -\frac{1}{V} \overline{P}(V, T) - \frac{l}{fV} \frac{\partial}{\partial V} \overline{\mathcal{H}(q)}.$$
(3.16)

Substituting Eqns (3.16) and (3.15) into Eqn (2.49) for the PFs, we finally get

$$\beta \overline{(\Delta P)^2} = -\frac{l}{fV} \frac{\partial}{\partial V} \overline{\mathcal{H}(q)} + \frac{1}{(fV)^2} \left[k^2 \overline{\mathcal{H}(p)} + l^2 \overline{\mathcal{H}(q)} \right].$$
(3.17)

For a comprehensive analysis of Eqn (3.17) one needs to know the explicit form of the kinetic and potential energies (or at least their indices of homogeneity), and the mean values of these energies.

Ideal gas. In the simplest case, when the potential energy of interaction between the particles is absent, and the macrosystem is an ideal gas, expressions (3.12) and (3.13) for DEOS-I and DEOS-II are simplified:

$$P_{V}(p) = \frac{k}{fV} \mathcal{H}(p), \quad \mathcal{H}(q) \equiv 0, \quad \mathcal{H}(p) = \mathcal{H}(p,q), \quad (3.18)$$
$$\Psi_{V}(p) = \frac{1}{V} P_{V}(p) + \left(\frac{k}{fV}\right)^{2} \mathcal{H}(p) = \frac{1}{V} \left(1 + \frac{k}{f}\right) P_{V}(p). \quad (3.19)$$

Accordingly, expressions (3.14) and (3.15) for TDEOS-I and TDEOS-II become

$$\overline{P}(V,T) = \frac{k}{fV} \overline{\mathcal{H}(p)}, \quad \chi_T^{(P)} = \frac{\partial \overline{P}(V,T)}{\partial V} = -\frac{\overline{P}(V,T)}{V}, \quad (3.20)$$
$$\overline{\Psi}(V,T) = \frac{1}{V} \left(1 + \frac{k}{f}\right) \overline{P}(V,T) = \frac{k}{fV^2} \left(1 + \frac{k}{f}\right) \overline{\mathcal{H}(p)}. \quad (3.21)$$

Expression (3.17) for the PFs in the case of an ideal gas goes over into

$$\beta \overline{(\Delta P)^2} = \frac{k\overline{P}}{fV} = \frac{\overline{P}^2}{\overline{\mathcal{H}(p)}}, \quad \left[\xi_P^2\right]^G \equiv \frac{\overline{(\Delta P)^2}}{\overline{P}^2} = \frac{1}{\beta} \frac{1}{\overline{\mathcal{H}(p)}}.$$
(3.22)

The mean values that enter Eqns (3.20) - (3.22) are calculated in Section 3.3.

²² For example, the values k = 1 and k = 2 correspond to a gas of ultrarelativistic or nonrelativistic particles, whereas l = -1 and l = 2 correspond to such interaction potentials as Coulomb and gravitational (l = -1) or quasi-elastic (l = 2) ones. We do not discuss here the problem of convergence of the integral (2.21) for these interactions.

Worthy of notice are the essential features important specifically for the case of an ideal gas. First of all, in this case the nonthermodynamic average $\Psi_V(p)$ becomes a thermodynamic average, because it is expressed in terms of the mean pressure $\overline{P_V(p)}$ or the mean kinetic energy $\overline{\mathcal{H}}(p)$ (which in this event coincides with the total internal energy $\overline{\mathcal{H}}$). Secondly, the presentation of DEOS-I in the form (3.18) gives us another way of calculating PFs, independent of the way outlined earlier in Eqn (2.49). Indeed, considering within the framework of the Gibbs approach the quantities \mathcal{H} and Pas random variables which are linked together, according to Eqn (3.18), by a linear dependence, we get

$$\left[\xi_P^2\right]^{\mathbf{G}} = \left[\xi_{\mathcal{H}}^2\right]^{\mathbf{G}} = \frac{\overline{\left(\Delta\mathcal{H}\right)^2}}{\overline{\mathcal{H}}^2} \,. \tag{3.23}$$

Here we have used the property of relative variances known from the probability theory (see, for example, Ref. [38]):

$$\xi_{aX}^2 = \xi_X^2, \quad a \neq 0, \tag{3.24}$$

where X is an arbitrary random quantity, and a is an arbitrary nonzero constant number (in this case $X = \mathcal{H}$, $a = V^{-1}k/f$). In this way, the calculation of PFs in the particular case of an ideal gas is reduced to the calculation of energy fluctuations, which gives an indirect solution of the Gibbs problem and allows us (in this case only) to avoid its straightforward solution.

3.2 DEOS in the quantum description. Generalization of the Hellmann-Feynman theorem

The procedure for development of DEOS and TDEOS in the case of the quantum description is generally the same as that in the classical case, save for the mathematical formalism. First of all, it would be natural to retain the definitions of the form (2.15) and (2.16) for the quantum counterparts of the quantities $\tilde{P}_{V}^{(0)}(\Gamma)$ and $\tilde{\Psi}_{V}^{(0)}(\Gamma)$ —that is, *the quasi-operators* of pressure and compressibility, respectively:

$$\widehat{P}_{V}^{(0)} = \lim_{\varepsilon \to 0} \widehat{P}_{V}^{(\varepsilon)} = \lim_{\varepsilon \to 0} \left(-\frac{\partial \widehat{\mathcal{H}}_{V}^{(\varepsilon)}}{\partial V} \right), \qquad (3.25)$$

$$\widehat{\Psi}_{V}^{(0)} = \lim_{\varepsilon \to 0} \widehat{\Psi}_{V}^{(\varepsilon)} = \lim_{\varepsilon \to 0} \left(-\frac{\partial \widehat{P}_{V}^{(\varepsilon)}}{\partial V} \right) = \lim_{\varepsilon \to 0} \frac{\partial^{2} \widehat{\mathcal{H}}_{V}^{(\varepsilon)}}{\partial V^{2}}, \quad (3.26)$$

where the Hamiltonian $\widehat{\mathcal{H}}_{V}^{(\varepsilon)}$ is given by Eqn (2.14).

Obviously, the derivation of quantum DEOS [that is, the explicit forms of the right-hand sides of Eqns (3.25) and (3.26)], reduces to the calculation of the derivatives of the Hamiltonian $\hat{\mathcal{H}}_{V}^{(\varepsilon)}$ with respect to the implicit parameter involved, the volume V. The definition of these quantities constitutes the generalized Hellmann–Feynman theorem proved independently in Refs [12, 13] when analyzing interactions in the molecules, and later [13] applied to the derivation of the quantum DEOS-II in the form (3.26) is concerned, to the best of our knowledge its development cannot be found in the scientific literature.

The Hellmann – Feynman theorem in the general form is formulated as follows (see, for example, Ref. [21]). Let $\hat{\mathcal{H}}$, $|n\rangle$, and E_n be the Hamiltonian, its eigenfunctions and eigenvalues (*n* is the set of quantum numbers), which depend on some parameter λ (which may be external or internal with respect to the system). The stationary Schrödinger equation takes the form

$$\widehat{\mathcal{H}}\left|n\right\rangle = E_{n}\left|n\right\rangle,\tag{3.27}$$

and its total variation is

~

$$\delta \widehat{\mathcal{H}} |n\rangle + \widehat{\mathcal{H}} |\delta n\rangle = \delta E_n |n\rangle + E_n |\delta n\rangle . \qquad (3.28)$$

Multiplying Eqn (3.28) from the left by $\langle n|$, and accounting for the normalization condition $\langle n|n \rangle = 1$, we find

$$\langle n|\delta \mathcal{H}|n\rangle + \langle n|\mathcal{H}|\delta n\rangle = \delta E_n + E_n \langle n|\delta n\rangle.$$

Now using the Hermitian property, $\widehat{\mathcal{H}}^+ = \widehat{\mathcal{H}}$, according to which one has

$$\langle n|\mathcal{H}^+ = \langle n|\mathcal{H} = E_n\langle n|,$$

we get the linkage between variations of the Hamiltonian $\delta \hat{\mathcal{H}}$ and variations of eigenvalues δE_n :

$$\langle n|\delta\hat{\mathcal{H}}|n\rangle = \delta E_n \,. \tag{3.29}$$

If these variations are caused by the change of a certain parameter λ , then Eqn (3.29) becomes a relation between the first derivatives ²⁴ of $\hat{\mathcal{H}}$ and E_n with respect to λ :

$$\left\langle n \left| \frac{\delta \hat{\mathcal{H}}}{\delta \lambda} \right| n \right\rangle = \frac{\delta E_n}{\delta \lambda} \,, \tag{3.30}$$

which completes the formulation of the Hellmann – Feynman theorem.

As a rule, the Hellmann–Feynman theorem is applied 'from left to right', which corresponds to the situation when the parameter λ enters $\hat{\mathcal{H}}$ explicitly. This theorem, however, can also be used 'from right to left', which may be interpreted as *the definition* of operator $\delta \hat{\mathcal{H}} / \delta \lambda$. Such a situation is encountered when the dependence $E_n(\lambda)$ arises because of the appropriate dependence $|n(\lambda)\rangle$, but through the boundary conditions or other auxiliary conditions rather than through the Hamiltonian $\hat{\mathcal{H}}^{25}$.

It is this second situation that takes place in the case of interest, when $\lambda = -V$, and the initial equation (3.27) with the Hamiltonian $\widehat{\mathcal{H}}_{V}^{(\varepsilon)}$ from formula (2.14) becomes

$$\widehat{\mathcal{H}}_{V}^{(\varepsilon)}|n\rangle = \left(\widehat{\mathcal{H}}^{(0)} + \varepsilon U_{V}\right)|n\rangle = \widehat{\mathcal{H}}^{(0)}|n\rangle_{V} = E_{n}(V)|n\rangle_{V}.$$
(3.31)

Here, the term $\varepsilon U_V(q)$ with any $\varepsilon > 0$ acts as the operator of projection from the entire space of states $|n\rangle$ (the eigenfunctions of $\widehat{\mathcal{H}}^{(0)}$ for a free system) onto the subspace of states $|n\rangle_V$, which satisfy the boundary condition of vanishing on the surface of an *f*-dimensional box of volume *V*:

$$|n\rangle_V = 0, \quad q_i^{(\alpha)} \in \{q\}^{(11)},$$
(3.32)

where $q_i^{(\alpha)}$ is any of the *f* coordinates of any of *N* particles.

²⁴ In spite of the intuitive 'obviousness' of the result (3.29), it is by no means trivial, because the variation of the Hamiltonian $\widehat{\mathcal{H}}$ only involves the eigenvalues E_n , whereas the eigenstates $|n\rangle$ seem to be not involved (actually, variations of $|n\rangle$ are 'swallowed' because $\widehat{\mathcal{H}}$ is an Hermitian operator).

²⁵ Of course, the definition of operator $\delta \hat{\mathcal{H}}/\delta \lambda$ obtained in this way is not universal and is good only for the particular problem in question.

Applying the procedure described above to the Schrödinger equation (3.31), and using definition (3.25), for the quasioperator of pressure (or, to be more precise, its quantummechanical mean value) we find the expression

$$\left\langle n \middle| \widehat{P}_{V}^{(0)} \middle| n \right\rangle_{V} = -\frac{\partial E_{n}(V)}{\partial V} , \qquad (3.33)$$

which acts as the quantum DEOS-I used in Ref. [13]. It is clear that the operator $\hat{P}_V^{(0)}$ in Eqn (3.33) is only defined on the subspace of states that satisfy condition (3.32).

To find the quasi-operator of compressibility (3.26), we need to calculate the second variation of the Schrödinger equation (3.31). Varying equation (3.28), again using the normalization condition and the Hermitian property, and assuming that

 $\delta \widehat{\mathcal{H}} \left| \delta n \right\rangle = \delta E_n \left| \delta n \right\rangle,$

by analogy with Eqn (3.29) we have

$$\langle n|\,\delta^2\,\widehat{\mathcal{H}}\,|n\rangle = \delta^2 E_n \tag{3.34}$$

or, dividing equality (3.34) by $(\delta \lambda)^2$, obtain

$$\left\langle n \left| \frac{\delta^2 \hat{\mathcal{H}}}{\delta \lambda^2} \right| n \right\rangle = \frac{\delta^2 E_n}{\delta \lambda^2} \,. \tag{3.35}$$

For our case of relation (3.31), we get the quantum DEOS-II in the from

$$\left\langle n \middle| \widehat{\Psi}_{V}^{(0)} \middle| n \right\rangle_{V} = \frac{\partial^{2} E_{n}(V)}{\partial V^{2}} , \qquad (3.36)$$

which is not found in Refs [12, 13]. Of course, the explicit forms of quantum DEOS (3.33) and (3.36) can only be found in the 'solvable' cases, when the dependence on the volume V of the eigenvalues $E_n(V)$ of the Hamiltonian $\hat{\mathcal{H}}^{(0)}$ for the eigenfunctions $|n\rangle_V$ is known.

Ideal gas. In the case of an ideal gas, the Hamiltonian $\hat{\mathcal{H}}^{(0)}$ contains only the term corresponding to the kinetic energy; it is therefore additive and depends only on the operators of microparticle momenta $\hat{p}_i^{(\alpha)} = -i\hbar\partial/\partial q_i^{(\alpha)}$, where $\alpha = 1, ..., f$, and i = 1, ..., N. For the nonrelativistic case (k = 2, m is the mass of microparticle) one obtains

$$\widehat{\mathcal{H}}^{(0)} = \sum_{i=1}^{N} \mathcal{H}_{i}^{(0)}, \quad \widehat{\mathcal{H}}_{i}^{(0)} = \frac{1}{2m} \sum_{\alpha=1}^{f} (\hat{p}_{i}^{(\alpha)})^{2}, \quad (3.37)$$

so that the problem of finding $|n\rangle$ and E_n is a one-particle problem. Then in Schrödinger's q-representation we have

$$\widehat{\mathcal{H}}_{i}^{(0)} | n_{i} \rangle_{V} = E_{n_{i}}(V) | n_{i} \rangle_{V},$$

where

$$|n_i\rangle_V = \left(\frac{2}{L}\right)^{f/2} \prod_{\alpha=1}^f \sin\frac{2\pi n_i^{(\alpha)}}{L} q_i^{(\alpha)}.$$
 (3.38)

Here, the numbers $\{n_i^{(\alpha)}\}$ run independently through all positive integers, and $L = V^{1/f}$ is the fixed edge length of an *f*-dimensional cubic box of volume *V*. Obviously, function (3.38) becomes zero when any of the coordinates $q_i^{(\alpha)}$ of any particle *i* hits the surface of one of the walls of the box along any of the α axes of the Cartesian coordinate system, when $q_i^{(\alpha)} = \pm L/2$.

Confining the consideration mainly to the nondegenerate regime $(T \ge T_0)$, we may disregard the quantum identity of microparticles²⁶, and represent the total wave function of the system as a simple (not symmetrized or antisymmetrized) product of functions of the type (3.38), and the eigenvalues as the appropriate sums:

$$|n\rangle_{V} = \prod_{i=1}^{N} |n_{i}\rangle_{V}, \quad E_{n}(V) = \sum_{i=1}^{N} E_{n_{i}}(V),$$
$$E_{n_{i}} = E_{1} \sum_{\alpha=1}^{f} (n_{i}^{(\alpha)})^{2}, \quad E_{1} \equiv \frac{1}{2m} \left(\frac{\pi\hbar}{L}\right)^{2}.$$
(3.39)

Here E_1 has the meaning of the ground state energy (all $n_i^{(\alpha)} = 1$) in the case of one-dimensional motion of any particle *i* along any coordinate α .

It is easy to see that, according to Eqn (3.39), the following relation holds good:

$$E_n(V) \propto E_1(V) \propto V^{-2/f}, \qquad (3.40)$$

so that

$$\frac{\partial E_n(V)}{\partial V} \propto \frac{\partial E_1(V)}{\partial V} \propto \left(-\frac{2}{f}\right) V^{-(2/f+1)} \propto \left(-\frac{2}{f}\right) \frac{1}{V} V^{-2/f}.$$
(3.41)

Using Eqn (3.41), from formulas (3.39) we find

$$-\frac{\partial E_n(V)}{\partial V} = \frac{2}{f} \frac{1}{V} E_n(V), \quad \frac{\partial^2 E_n(V)}{\partial V^2} = \left(\frac{2}{f} + 1\right) \frac{1}{V} \frac{\partial E_n(V)}{\partial V}.$$
(3.42)

Using definitions (3.33) and (3.36) and equations (3.42), we finally get the quantum DEOS-I and DEOS-II:

$$\widehat{P}_{V}^{(0)} = \frac{2}{fV} \,\widehat{\mathcal{H}}^{(0)}, \quad \widehat{\Psi}_{V}^{(0)} = \left(\frac{2}{f} + 1\right) \frac{1}{V} \,\widehat{P}_{V}^{(0)}. \tag{3.43}$$

It is easy to see that these equations are exact quantum analogs (in the spirit of the correspondence principle) of the classical DEOS (3.18) and (3.19). This means that all relations for the mean values and fluctuations (3.20) - (3.23), obtained in the classical description, remain valid.

Observe that, according to Eqns (3.18) and (3.43), in the case of an ideal gas there is a simple relationship between the thermal (for \overline{P}) and caloric (for \overline{H}) TDEOS, in both the classical and quantum descriptions:

$$\overline{P} = \frac{2}{f} \frac{1}{V} \overline{\mathcal{H}}.$$
(3.44)

The last linkage retains its form over the entire range of values of V and T: both well above the temperature $T_0(V)$ for which it was obtained, and around or below this temperature (see, for example, Refs [7, 21]). It is important that the expressions for the quantities \overline{P} and $\overline{\mathcal{H}}$ as such exhibit a dramatic change (for example, quantum exchange corrections appear in the form of expansions in powers of T_0/T ; see Refs [7, 21, 26]).



3.3 TDEOS and PFs for an ideal gas in the nondegenerate regime. Solution of the Gibbs problem

Classical description. The derivation of classical TDEOS-I and TDEOS-II [expressions (3.20) and (3.21), respectively] as functions of temperature *T* and volume *V* obviously requires knowing the mean values of pressure \overline{P} or (only in the case of an ideal gas) the mean energy $\overline{\mathcal{H}}(p) = \overline{\mathcal{H}}$. For this, it is sufficient to calculate the statistical integral (2.21) and the Massieu – Planck function (2.22): its derivatives, according to Eqns (2.30), (2.31) and (2.47), will define $\overline{P}, \overline{\mathcal{H}}$, and $(\overline{\Delta \mathcal{H}})^2$. In the case of an ideal gas this will provide the possibility of finding PFs by both methods described at the end of Section 3.1.

Confining ourselves to the case of k = 2 (an ideal gas of nonrelativistic particles), for the Hamiltonian function we have

$$\mathcal{H}(p) = \sum_{i=1}^{N} \sum_{\alpha=1}^{f} \frac{1}{2m} \left(p_i^{(\alpha)} \right)^2.$$
(3.45)

The additivity of $\mathcal{H}(p)$ leads to multiplicativity of the statistical integral ²⁷

$$\mathcal{Z}_{\mathcal{C}}(\beta, V) = \left[\widetilde{\mathcal{Z}}_{\mathcal{C}}(\beta, V)\right]^{fN}.$$
(3.46)

The statistical integral in Eqn (3.46) for each of the f translational degrees of freedom for one particle may be represented as a product of two terms:

$$\widetilde{\mathcal{Z}}_{\mathcal{C}}(\beta, V) = (2\pi\hbar)^{-1} \widetilde{\mathcal{Z}}_p(\beta) \widetilde{\mathcal{Z}}_q(V) = \beta^{-1/2} V^{1/f} b, \quad (3.47)$$

where $b = c/2\pi\hbar$, and $c = (2\pi m)^{1/2}$ are constants. Here we have used the fact that for any values of i = 1, ..., N and $\alpha = 1, ..., f$, and with due account for the domains of integration (2.5), the terms entering Eqn (3.47) are

$$\begin{split} \widetilde{\mathcal{Z}}_p(\beta) &= \int_{-\infty}^{\infty} \mathrm{d} p_i^{(\alpha)} \exp\left[-\beta \, \frac{(p_i^{(\alpha)})^2}{2m}\right] = \beta^{-1/2} c\\ \widetilde{\mathcal{Z}}_q(V) &= \int_{-L/2}^{L/2} \mathrm{d} q_i^{(\alpha)} = L = V^{1/f}. \end{split}$$

The Massieu–Planck function, which corresponds to the classical description of the ideal gas, with due account for formulas (3.46) and (3.47) (up to the constant $N \ln b$ which in the present case can be considered insignificant) is given by

$$\Phi_{\rm C}(\beta, V) = \ln \mathcal{Z}_{\rm C}(\beta, V) = N \left[-\frac{f}{2} \ln \beta + \ln V \right].$$
(3.48)

The thermal TDEOS-I in this case constitutes the *Clapeyron – Mendeleev equation*

$$\overline{P} = \frac{1}{\beta} \frac{\partial \Phi(\beta, V)}{\partial V} = \frac{1}{\beta} \frac{N}{V} = \frac{Nk_{\rm B}T}{V} \,. \tag{3.49}$$

According to the last relationship, the isothermal compressibility takes the from

$$\chi_T^{(P)} = \frac{\partial \overline{P}}{\partial V} = -\frac{Nk_{\rm B}T}{V^2} = -\frac{\overline{P}}{V}, \qquad (3.50)$$

²⁷ To facilitate comparison with the results of Section 3.2, we drop the factor 1/N! which is necessary in the general case, since in the quantum description the simple product of one-particle wave functions is used without regard for the symmetry requirements.

and the thermal pressure coefficient is

$$\chi_V^{(P)} = \frac{\partial \overline{P}}{\partial T} = \frac{Nk_{\rm B}}{V} = \frac{\overline{P}}{T} \,. \tag{3.51}$$

Accordingly, for the thermal TDEOS-II we get

$$\overline{\Psi} = \left(\frac{2}{f} + 1\right) \,\overline{\frac{P}{V}} = -\left(\frac{2}{f} + 1\right) \chi_T^{(P)} \,. \tag{3.52}$$

The caloric TDEOS is written in the following way

$$\overline{\mathcal{H}} = -\frac{\partial \Phi(\beta, V)}{\partial \beta} = N \frac{f}{2} \frac{1}{\beta} = C_V T, \qquad (3.53)$$

where the heat capacity at constant volume is

$$C_V = \frac{\partial \overline{\mathcal{H}}}{\partial T} = N \frac{f}{2} k_{\rm B} \tag{3.54}$$

and defines, according to Eqn (2.47), not only the mean energy (3.53), but also its variance

$$\overline{(\Delta \mathcal{H})^2}^{\rm G} = \frac{\partial^2 \Phi(\beta, V)}{\partial \beta^2} = \frac{1}{k_{\rm B} \beta^2} C_V = N \frac{f}{2} \frac{1}{\beta^2} .$$
(3.55)

As far as the quantity $[\xi_P^2]^G$ is concerned (or PFs according to Gibbs), it can be found by two independent methods as shown at the end of Section 3.1:

(a) according to Eqn (3.22)

$$\left[\xi_{P}^{2}\right]^{G} = \frac{1}{\beta} \frac{1}{\overline{\mathcal{H}}} = \frac{k_{B}}{C_{V}} = \frac{2}{f} \frac{1}{N}, \qquad (3.56)$$

(b) according to Eqn (3.23)

$$\left[\xi_P^2\right]^{\rm G} = \left[\xi_{\mathcal{H}}^2\right]^{\rm G} = \frac{\left(\Delta\mathcal{H}\right)^2}{\overline{\mathcal{H}}^2} = \frac{k_{\rm B}}{C_V} = \frac{2}{f} \frac{1}{N}.$$
(3.57)

Needless to say that the results of calculation of PFs according to Gibbs by both methods are the same.

Quantum description. In complete analogy with the classical description, in this case we have to find the partition function (statistical sum)

$$\mathcal{Z}_{Q}(\beta, V) = \sum_{n} \exp\left[-\beta E_{n}(V)\right],$$

where the energy eigenvalues $E_n(V)$ are given by formulas (3.39). Because $E_n(V)$ is additive with respect to *i* and α , the statistical sum $\mathcal{Z}_Q(\beta, V)$ [just like $\mathcal{Z}_C(\beta, V)$ from Eqn (3.46)] can be represented multiplicatively in terms of the statistical sum per degree of freedom:

$$\widetilde{\mathcal{Z}}_{\mathbf{Q}}(\beta, V) \equiv \sum_{n_i^{(\alpha)}=1}^{\infty} \exp\left[-\beta E_1(V)(n_i^{(\alpha)})^2\right].$$
(3.58a)

The quantity (3.58a), unlike quantity (3.47), cannot be represented as a product. In the limit of large values of *L*, characteristic of the macrosystem, the spectrum (3.39) becomes quasi-continuous, and the summation in formula (3.58a) can be replaced by integration:

$$\widetilde{\mathcal{Z}}_{Q}(\beta, V) = \int_{0}^{\infty} dn_{i}^{(\alpha)} \exp\left[-\beta E_{1}(V)(n_{i}^{(\alpha)})^{2}\right]$$
$$= \frac{\sqrt{\pi}}{2} \left[\beta E_{1}(V)\right]^{-1/2},$$

so that we finally get

$$\begin{aligned} \widetilde{\mathcal{Z}}_{Q}(\beta, V) &= \beta^{-1/2} V^{1/f} b = \widetilde{\mathcal{Z}}_{C}(\beta, V), \\ \Phi_{Q}(\beta, V) &= \Phi_{C}(\beta, V). \end{aligned}$$
(3.58b)

Since the Massieu – Planck function in the quantum description exactly coincides with its classical counterpart (3.48), all relations (3.49) - (3.57) characteristic of the classical description also remain valid for the quantum description (neglecting the exchange effects).

To conclude this section, we observe that in the particular case of an ideal gas the solution of the Gibbs problem — that is, the expression for the nonthermodynamic quantity $\overline{\Psi}$ looks especially simple. Using the Mayer relation for this case, $C_P = C_V + Nk_B$, the factor 2/f + 1 has the meaning of the Poisson coefficient $\gamma = C_P/C_V$, so that expression (3.52) can be written as follows

$$\overline{\Psi} = -\gamma \chi_T^{(P)} = -\chi_S^{(P)}, \quad \gamma = \frac{C_P}{C_V} = \frac{2}{f} + 1 > 1.$$
 (3.59)

According to the initial definition (1.2) [see also Eqn (2.49)], we have

$$\overline{(\Delta P)^2}^{\rm G} = \frac{1}{\beta} \left[\chi_T^{(P)} - \chi_S^{(P)} \right] = -\frac{1}{\beta} (\gamma - 1) \chi_T^{(P)} \,. \tag{3.60}$$

Taking Eqn (1.7) into account we clearly see that

$$\overline{\left(\Delta P\right)^{2}}^{\mathrm{E}} - \overline{\left(\Delta P\right)^{2}}^{\mathrm{G}} = -\frac{1}{\beta} \chi_{T}^{(P)} > 0.$$
(3.61)

In this way, Einstein's problem as applied to the ideal gas acquires a more concrete meaning. Indeed, substituting relation (3.50) into Eqn (3.61) and taking equation (3.49) into account, we get

$$\left[\xi_P^2\right]^{\rm E} - \left[\xi_P^2\right]^{\rm G} = \frac{1}{N} > 0.$$
(3.62)

Observe that the discussion of the physical meaning of this simple relation is only possible on the basis of comparison of the Gibbs and Einstein approaches as the whole (see Section 4). Such a comparison is drawn in Section 5.2.

4. Main elements of Einstein's approach and its 'genetic' linkage with the Gibbs approach

Let us now proceed to the more precise formulation and analysis of Einstein's problem for PFs, which, in our opinion, is deeper and more substantial than the Gibbs problem considered earlier in Section 3. The analysis of Einstein's problem paves the way towards a more comprehensive (and probably more adequate to physical reality) description of fluctuations of macroparameters that characterize *stochastic macroscopic* objects in quasi-equilibrium states. Following mainly Ref. [11] (see also Refs [20, 36]) we shall discuss the conceptual basics of the Einstein statistical thermodynamics [3], and especially its 'genetic' linkage with the Gibbs statistical mechanics [2], in somewhat greater detail than is needed for solving the concrete problem of pressure fluctuations.

4.1 Mean values and fluctuations of G-variables in the generalized Gibbs ensemble

The starting point for the construction of Einstein's approach [3], according to Ref. [11], may be the normalized classical (not quantum) Gibbs distribution function.

For *the generalized Gibbs ensemble*, this function can be written with the help of the so-called *F*-parametrization (the particular case with $F_1 = \beta$, $P_1(\Gamma) = \mathcal{H}(\Gamma)$ was considered in Section 2):

$$\rho^{\mathrm{G}}(\Gamma; \{F_i\}) = \exp\left[-\Phi\{F_i\} - \sum_k F_k P_k(\Gamma)\right].$$
(4.1)

Physically, the generalized Gibbs ensemble corresponds to a given type of the macrosystem thermodynamic contact with the environment; the quantities F_k include, for example, the inverse temperature β , as well as the pressure P and the chemical potential μ (in units of β).

The distribution function (4.1) can be used for calculating all the mean values of the extensive physical quantities $\overline{P_k(\Gamma)}$ and correlators $\overline{P_k(\Gamma)P_l(\Gamma)}$, which characterize the Gibbs approach, as functions of the intensive physical quantities $\{F_i\}$. According to Gibbs [2] (see also Ref. [11]), it is also useful to introduce the *phase index*

$$\eta^{G}(\Gamma; \{F_i\}) \equiv -\ln \rho^{G}(\Gamma; \{F_i\}) = \Phi\{F_i\} + \sum_k F_k P_k(\Gamma),$$
(4.2)

which, like $\rho^{G}(\Gamma; \{F_i\})$, presents a quantity of 'mixed nature'.

Similar to the dynamic variables, the quantities ρ^{G} and η^{G} are defined over the phase space Γ ; at the same time, like the thermodynamic quantities they depend on parameters $\{F_i\}$. It is important that the mean value of the phase index coincides (up to a coefficient $k_{\rm B}$) with the thermodynamic entropy:

$$\overline{\eta^{G}(\Gamma; \{F_i\})} \equiv \frac{1}{k_{\rm B}} S\{\overline{P}_i\} = \Phi\{F_i\} + \sum_k F_k \overline{P}_k \,. \tag{4.3}$$

The status of quantities $P_k(\Gamma)$ and F_k in Eqns (4.1) and (4.2) is essentially different ²⁸. The quantities $P_k(\Gamma)$ are random dynamic variables defined over the phase space $\{\Gamma\}$ of the macrosystem under consideration (they usually include the extensive quantities like energy \mathcal{H} , volume V, and number of particles N).

By contrast, the quantities F_k are neither dynamic nor random: they do not depend on the argument Γ , and uniquely characterize the Gibbs ensemble as a whole. The quantities F_k , like the ensemble averages $\overline{P_k(\Gamma)}$, are essentially thermodynamic rather than dynamic variables. In the Gibbs approach, the quantities F_k have strictly defined values (for given physical conditions) that are the same for the object and the thermostat.

Simplifying a little, we can say that the main idea of Einstein's approach consists in 'equalizing' the status of quantities $P_k(\Gamma)$ and F_k , which characterize the Gibbs approach, and giving both of them the meaning of *random*

²⁸ As will be shown below, $\{F_i\}$ are the analog of the quantities $\{x\}$, and $\{P_i\}$ are the analog of the quantities $\{D_x\}$ from Section 2.3 (except for the conjugate volume-pressure pair, which cannot be introduced in the isochoric situation in the form (4.1); see Section 2.2).

thermodynamic variables. To do this, one has to 'detach' the quantities $P_k(\Gamma)$ from the phase space $\{\Gamma\}$, leaving them the 'privilege' to fluctuate about \overline{P}_k , and also 'allowing' the quantities F_k (which previously had been uniquely related to \overline{P}_k) to fluctuate. The realization of this idea is described in Section 4.2; in this section we consider fluctuations and correlations within the framework of the Gibbs approach for an ensemble more general than the canonical one (in Sections 2.3 and 2.4).

The quantities F_k and \overline{P}_k are thermodynamically conjugated because, as follows from Eqn (4.1), the generating function for \overline{P}_k is the Massieu–Planck function $\Phi\{F_i\}$. Indeed, one obtains

$$\overline{P}_k = -\frac{\partial \Phi\{F_i\}}{\partial F_k}, \quad \overline{P}_k = \overline{P}_k\{F_i\}, \quad (4.4)$$

so that \overline{P}_k , similarly to \overline{D}_x from Section 2.3, are thermodynamic averages.

Accordingly, for F_k the generating function is the entropy $S\{\overline{P}_i\}$, so that

$$F_k = \frac{1}{k_{\rm B}} \frac{\partial S\{\overline{P}_i\}}{\partial \overline{P}_k}, \quad F_k = F_k\{\overline{P}_i\}.$$
(4.5)

Here we have taken into account that, by virtue of definition (4.3), the quantities $S\{\overline{P}_i\}$ and $\Phi\{F_i\}$ are linked through the Legendre transformation. Relation (4.5) together with (4.3) allows going over in the Gibbs distribution function from *F*-parametrization (4.1) to \overline{P} -parametrization

$$\rho^{\rm G}(\Gamma; \{\overline{P}_i\}) = \exp\left[-\frac{1}{k_{\rm B}}S\{\overline{P}_i\} - \sum_k F_k\{\overline{P}_i\}\Delta P_k^{\rm G}(\Gamma)\right].$$
(4.6)

Function (4.6), like that in Eqn (4.1), remains normalized ²⁹, but now it is more convenient for the subsequent transition from the Gibbs approach to the Einstein approach. In writing Eqn (4.6) we have used the definition of linear deviations (fluctuations) of dynamic quantities $P_k(\Gamma)$ from their mean values \overline{P}_k :

$$\Delta P_k^{\rm G}(\Gamma) \equiv P_k(\Gamma) - \overline{P}_k \,. \tag{4.7}$$

Generally speaking, fluctuations (4.7) are nonzero; the only exception is the Boltzmann case or the microcanonical ensemble with respect to all variables P_k , when all quantities $P_k(\Gamma)$ (as a rule, the integrals of motion of the system) are defined exactly rather than on the average:

$$\Delta P_k^{\mathbf{B}}(\Gamma) \equiv 0, \quad P_k^{\mathbf{B}}(\Gamma) \equiv P_k.$$
(4.8)

In this case the Gibbs distribution function (4.6) becomes a constant and coincides with the Boltzmann distribution function $\rho^{B}\{P_{i}\}$:

$$\rho^{\mathcal{G}}\{P_i\} \equiv \rho^{\mathcal{B}}\{P_i\} = \exp\left[-\frac{1}{k_{\mathcal{B}}}S\{P_i\}\right].$$
(4.9)

²⁹ It will be useful to note that, from the standpoint of variation properties, Eqn (4.1) corresponds to the unconditional minimum of function Φ , whereas Eqn (4.6) corresponds to the conditional minimum of function *S*; the linkage between these functions is given by Eqn (4.3). It is easy to see that the last formula is an alternative presentation of the known *Boltzmann formula*

$$S = k_{\rm B} \ln W, \quad W = \frac{1}{\rho} \tag{4.10}$$

for an isolated macrosystem in the state of thermodynamic equilibrium, where W is the statistical weight, and ρ is the probability of this state.

In the general case, when the fluctuations (4.7) are nonzero, we have an obvious equality

$$\overline{\Delta P_k^{\rm G}(\Gamma)} \equiv 0\,,\tag{4.11}$$

so that the ensemble-average measure of fluctuations of dynamic quantities $P_k(\Gamma)$ is the pair correlation function (which in the particular case of k = l coincides with the absolute variance):

$$\overline{\Delta P_k^{\mathbf{G}}(\Gamma) \,\Delta P_l^{\mathbf{G}}(\Gamma)} \equiv \overline{\Delta P_k(\Gamma) \,\Delta P_l(\Gamma)}^{\mathbf{G}} = \varphi_{kl} \,. \tag{4.12}$$

It is easy to obtain formula (4.12) by differentiating expression (4.4) for the mean values. Here $\varphi_{kl} = \varphi_{lk}$ is a symmetrical positive-definite (which follows from the condition of absolute minimum for $\Phi\{F_i\}$) matrix of generalized susceptibilities:

$$\varphi_{kl} = -\frac{\partial \overline{P}_k}{\partial F_l} = -\frac{\partial \overline{P}_l}{\partial F_k} = \frac{\partial^2 \Phi\{F_i\}}{\partial F_l \partial F_k} .$$
(4.13)

Formula (4.12) is a particular case of expression (2.41) when $\chi \neq 0$, $\psi \equiv 0$, since the variables $\{P_i(\Gamma)\}$ by definition do not depend on $\{F_i\}$, and $\{F_i\}$ themselves by assumption are independent of one another ³⁰. Obviously, the relations for F_k similar to formula (4.12) in the Gibbs approach would have been meaningless from the outset, because by definition

$$\Delta F_k^{\mathbf{G}} \equiv 0, \qquad (4.14)$$

and, unlike $P_k(\Gamma)$, the quantities F_k cannot fluctuate ³¹.

In this connection it is worthwhile to note the following important circumstance. As follows from relations (4.7) and (4.12), the concept of a random quantity (and its fluctuation) in the Gibbs approach is only applicable to the dynamic quantities $P_k(\Gamma)$ that depend on the argument Γ . The concept of fluctuation must not be confused with another entity employed in the Gibbs approach — the *quasi-static* (but not random!) small change or increment of the mean values \overline{P}_k (and hence F_k) in the course of equilibrium processes. To avoid confusion ³², we denote these increments as $\delta \overline{P}_k$ and δF_k . Obviously, by virtue of Eqns (4.4) and (4.5) they are linked by the linear relations

$$\delta \overline{P}_{k}^{\mathbf{G}} = -\sum_{l} \varphi_{kl} \,\delta F_{l}^{\mathbf{G}} \,, \quad \delta F_{k}^{\mathbf{G}} = \sum_{l} \sigma_{kl} \,\delta \overline{P}_{l}^{\mathbf{G}} \,. \tag{4.15}$$

³⁰ Violation of this assumption considerably complicates the formalism presented above (see Section 5).

³¹ In cases when it is the statistical behavior of F_k that is of interest, one must go over to the conjugate Gibbs ensemble, 'exchanging the roles' of quantities F_k and P_k .

³² In the scientific literature, as a rule, no distinction is made in the notation for increments δF_k and fluctuations ΔF_k , which may sometimes lead to misunderstanding.

The matrix of inverse generalized susceptibilities

$$\sigma_{kl} = \frac{\partial F_k}{\partial \overline{P}_l} = \frac{\partial F_l}{\partial \overline{P}_k} = \frac{1}{k_{\rm B}} \frac{\partial^2 S\{\overline{P}_l\}}{\partial \overline{P}_l \partial \overline{P}_k}, \qquad (4.16)$$

like the matrix φ_{kl} from Eqn (4.13), is symmetrical: $\sigma_{kl} = \sigma_{lk}$; but, unlike φ_{kl} , it is negative-definite (this follows from the requirement of conditional maximum for $S\{\overline{P}_i\}$ at the state of thermodynamic equilibrium).

It is easy to check that the matrices $(-\varphi_{kl}) \equiv -\hat{\varphi}$ and $\sigma_{lk} \equiv \hat{\sigma}$ are mutually inverse:

$$(-\hat{\varphi})\hat{\sigma} = 1, \quad -\hat{\sigma} = \hat{\varphi}^{-1}.$$
 (4.17)

To prove this, we use the obvious condition of 'orthogonality'

$$\frac{\partial \overline{P}_k}{\partial \overline{P}_l} = \delta_{kl} \tag{4.18}$$

and take advantage of the fact that the left-hand part of Eqn (4.18) with due account for Eqns (4.4) and (4.5) can be written as

$$\frac{\partial \overline{P}_k}{\partial \overline{P}_l} = \sum_m \frac{\partial \overline{P}_k}{\partial F_m} \frac{\partial F_m}{\partial \overline{P}_l} = \sum_m (-\varphi_{km}) \,\sigma_{ml} \,. \tag{4.19}$$

Comparison of the right-hand sides of Eqns (4.19) and (4.18) proves relationships (4.17).

4.2 'Stochastization' of thermodynamic parameters: from Gibbs to Einstein

So we see that the Gibbs approach [2] or *statistical mechanics* adequately describes thermodynamically *equilibrium* states of macrosystems, characterized by *fixed* values of thermodynamic quantities $\{\overline{P}_k\}$ (or, which is the same, $\{F_k\}$). According to Eqn (4.7), only the dynamic variables $\{P_k(\Gamma)\}$ can fluctuate in such states, while fluctuations of $\{\overline{P}_k\}$ and $\{F_k\}$ in the framework of the Gibbs approach are not possible in principle.

The description of *quasi-equilibrium* states of macrosystems, characterized by random deviations or *fluctuations* of $\{\overline{P}_k\}$ and $\{F_k\}$ from their equilibrium values, is realized in Einstein's approach [3] known as *statistical thermodynamics*. As demonstrated by Planck [6], Einstein's approach paves the way for an extension of the very concept of thermal equilibrium, and hence a generalization of the *zero principle of thermodynamics*. Planck's formulation differs from the conventional approach in that the intensive parameters of the macrosystem are allowed to fluctuate, while the same parameters of the thermostat are fixed ³³.

In this way, the random variable in Einstein's approach is not the dynamic but rather the thermodynamic quantity P_k , which fluctuates in quasi-equilibrium states. Formally this corresponds to the removal of the microscopic phase argument Γ in definition (4.7) of the fluctuation according to Gibbs, so that the fluctuation of macroscopic quantities P_k , or E-variables, according to Einstein is defined as

$$\Delta P_k^{\rm E} = P_k - \overline{P}_k \,. \tag{4.20}$$

³³ This issue is discussed in greater detail at the end of this section in connection with the generalized Boltzmann principle (see also the discussion in Refs [4, 5]).

With due account for expressions (4.4) and (4.5) it is evident that in these states the thermodynamic quantities F_k conjugated with \overline{P}_k also fluctuate. Then the 'genetic' linkage with the Gibbs approach is revealed by the fact that fluctuations of E-variables $\Delta F_k^{\rm E}$ and $\Delta P_k^{\rm E}$ according to Einstein [3] are linked by the same equilibrium relations (4.15) that hold for the increments $\delta F_k^{\rm G}$ and $\delta \overline{P}_k^{\rm G}$ according to Gibbs:

$$\Delta F_k^{\rm E} = \sum_l \sigma_{kl} \Delta P_l^{\rm E}, \qquad \Delta P_k^{\rm E} = -\sum_l \varphi_{kl} \Delta F_l^{\rm E}. \qquad (4.21)$$

Moreover, all equilibrium values of \overline{P}_k and F_k used in Einstein's approach and the matrices of thermodynamic derivatives φ_{kl} and σ_{kl} are either 'borrowed' from the Gibbs approach or introduced empirically. Despite the existence of such 'heredity', however, relations (4.20) and (4.21) symbolize the conceptual break between the Gibbs and Einstein approaches: one might figuratively say that according to Einstein the macrosystem is *more stochastic* than according to Gibbs (which is more in line with physical reality).

To wit, the Gibbs approach assumes that a *macroscopic measurement* performed on a macroscopic system at the state of thermal equilibrium yields a well-determined result for \overline{P}_k (and hence for F_k) — that is, fluctuations of these quantities do not exist. By contrast, Einstein's approach allows for some spread in the measured values of P_k , and accordingly in the thermodynamically conjugated values of F_k . This spread, as will be shown below, is characterized by the correlation functions ($k \neq l$) and variances (k = l) [see formulas (4.37) and (4.38)].

In this way, differently from the Gibbs approach, the approach of Einstein is mainly concerned not with the mean (equilibrium) values of \overline{P}_k and the corresponding values of F_k , but rather with the *quasi-equilibrium fluctuations* of these quantities (4.21). Accordingly, Einstein's approach is called the *quasi-thermodynamic fluctuation theory*, and the appropriate distribution function $\rho^{\rm E} \{\Delta P_i^{\rm E}\}$ can formally be constructed from distribution functions $\rho^{\rm G}(\Gamma; \{\overline{P}_i\})$ and $\rho^{\rm G}\{P_i\}$ [see Eqns (4.6) and (4.9)] in the following way

$$\rho^{\mathrm{E}}\{\Delta P_{i}^{\mathrm{E}}\} \equiv \frac{\rho^{\mathrm{G}}(\Gamma; \{\overline{P}_{i}\})}{\rho^{\mathrm{G}}\{P_{i}\}} \bigg|_{P_{i}(\Gamma) \to P_{i}}$$
$$= \exp\left[\frac{1}{k_{\mathrm{B}}}\Delta S\{\Delta P_{i}^{\mathrm{E}}\} - \sum_{k} F_{k}^{\mathrm{G}} \Delta P_{k}^{\mathrm{E}}\right]. \quad (4.22)$$

Here we have accounted for definition (4.20) and introduced the notation

$$\Delta S\{\Delta P_i^{\rm E}\} = S\{P_i\} - S\{\overline{P}_i\}$$
(4.23)

for the deviation of entropy from its conditional maximum value $S\{\overline{P}_i\}$, which characterizes the equilibrium state of the macrosystem in thermal contact with the thermostat.

By analogy with formula (4.2), it would be useful to consider the *phase index* that describes Einstein's quasi-equilibrium distribution function:

$$\eta^{\mathrm{E}}\{\Delta P_{i}^{\mathrm{E}}\} \equiv -\ln\rho^{\mathrm{E}}\{\Delta P_{i}^{\mathrm{E}}\} = \frac{1}{k_{\mathrm{B}}T}\Delta R\{\Delta P_{i}^{\mathrm{E}}\},\qquad(4.24)$$

where

$$R \equiv \frac{1}{\beta} \left\{ \sum_{k} F_{k}^{\mathrm{G}} P_{k}^{\mathrm{E}} - \frac{1}{k_{\mathrm{B}}} S \right\}, \qquad \Delta R \ge 0.$$
 (4.25)

By contrast to Eqn (4.2), the quantity (4.24) is purely *thermodynamic* rather than mixed, and has a relatively straightforward physical meaning.

According to Ref. [7], the quantity $\Delta R\{\Delta P_i^E\}$ is the smallest positive amount of work (see also Refs [14–17]) that must be done by any external source to change the macrosystem under consideration from the equilibrium state with $\{\Delta P_i^E\} \equiv 0, \Delta S = 0$ to the quasi-equilibrium or the fluctuative state) with $\{\Delta P_i^E\} \neq 0, \Delta S \neq 0$. In the course of this process the parameters of the thermostat are kept constant $(F_k^G = \text{const})$, while the parameters of the macrosystem, generally speaking, fluctuate in accordance with relations (4.21), so that $\{\Delta F_k^E\} \neq 0, F_k^E \neq F_k^G$. As indicated before, such a 'dissimilarity' between the macrosystem and thermostat [see formulas (4.30) and (4.31)] seems to open the possibility for a more deep insight into the nature of thermal equilibrium and the zero principle of thermodynamics.

In the special case when the intensive thermodynamic parameters of the system and the thermostat are the same $(F_k^{\rm E} = F_k^{\rm G})$, in the right-hand side of Eqn (4.25) we may use expression (4.3). Then the quantity

$$R = -\frac{1}{\beta} \Phi, \quad \Phi = \frac{1}{k_{\rm B}} S - \sum_{k} F_k P_k, \qquad (4.26)$$

where Φ is the Massieu–Planck function, coincides with the *characteristic function* or the thermodynamic potential corresponding to the given physical situation. For example, with k = 1, when $F_1 = \beta$ and $P_1 = \mathcal{H}$, the quantity $R = \mathcal{H} - TS$ is the free energy, while with k = 1, 2, when $F_2 = \beta P$, $P_2 = V$, the quantity $R = \mathcal{H} + PV - TS$ is the Gibbs thermodynamic potential, etc. In all these cases the inequality (4.25) expresses the property of stability of the thermal equilibrium state.

It is very important that the procedure of transition in formulas (4.22) from the Gibbs distribution function to the Einstein distribution function implies a radical change in the 'space of events' (in the sense of probability theory)³⁴. According to relations (4.22), we are dealing with the transition from the dynamic (or phase) space $\{\Gamma\}$ (with the admissible real values of variables *p* and *q* for the given system) to the *space of macroparameters*, in which the thermodynamic fluctuations $\{\Delta P_i^E\}$ are defined that may take on, generally speaking, any real values. Of course, such a transition violates the normalization condition for the initial distribution function (4.1) or (4.6), and the distribution function (4.22) has to be normalized anew.

Generalized Boltzmann principle. Einstein's original derivation [3] of the fluctuation distribution function for a 'small' (but macroscopic) object weakly interacting with a 'large' thermostat relied on the *generalized Boltzmann principle*. For the description of the *nonequilibrium* state of the complete system that consists of the object and the thermostat and is assumed isolated, in consistency with the common practice of thermodynamics, Einstein [3] (see also Ref. [6]) suggested starting with the Boltzmann distribution (4.9) for the *equilibrium* state of the whole system. In this case the sought distribution function, which has the meaning of the prob-

ability of the 'fluctuative' macroscopic state, becomes

$$\rho_{\text{whole}}^{\text{E}} = A \exp\left\{\frac{1}{k_{\text{B}}} \Delta S_{\text{whole}}\right\}.$$
(4.27)

It is essential that the quantity ΔS_{whole} (by definition, the change in entropy of the whole system) from the very beginning shows a purely thermodynamic, macroscopic sense. Given the presumed additivity of entropy of weakly interacting subsystems (object and thermostat), we have

$$\Delta S_{\rm whole} = \Delta S_{\rm ob} + \Delta S_{\rm th} \,, \tag{4.28}$$

with the result from the second law of thermodynamics:

$$\Delta S_{\text{whole}} \leqslant 0. \tag{4.29}$$

The sign of equality in Eqn (4.29) corresponds to the case when the state in question resides in the equilibrium state.

In the simplest case one may assume that the change in entropy (4.28) is due to the *spatially homogeneous* random variations (fluctuations) of both extensive (P_k) and intensive (F_k) thermodynamic variables characterizing the object and the thermostat. For quantities P_k there are exact relations that follow from the conservation laws for an isolated system:

$$(P_k)_{\rm th} + (P_k)_{\rm ob} = {\rm const}, \ (\Delta P_k)_{\rm th} = -(\Delta P_k)_{\rm ob}, \ (4.30)$$

while the approximate (up to the fluctuations of these quantities that describe the 'small' object) relations hold for the quantities F_k :

$$(F_k)_{\rm th} \approx (F_k)_{\rm ob} , \qquad (\Delta F_k)_{\rm th} = 0 ,$$

$$(\Delta F_k)_{\rm ob} \neq 0 , \qquad \frac{(\Delta F_k)_{\rm ob}}{(F_k)_{\rm ob}} \ll 1 .$$
(4.31)

The different treatment of fluctuations of variables F_k for the object and the thermostat is explained by the different degree of 'macroscopicity' of these subsystems: the thermostat is 'very large' compared with the object. Because of this, there is an additional small parameter $(\Delta F_k)_{\text{th}}/(\Delta F_k)_{\text{ob}} \sim (N_{\text{ob}}/N_{\text{th}})^{1/2} \ll 1$ that can be used in the description of the object and the thermostat at thermal equilibrium. Assuming that all changes in the thermostat are quasi-static (reversible), we use the first law of thermodynamics and eliminate fluctuations $(\Delta P_k)_{\text{th}}$ of the extensive quantities of the thermostat with the aid of Eqn (4.30), thus coming to the distribution function $\rho_{\text{ob}}^{\text{E}}$ in the form of Eqn (4.22).

Observe that a similar result [for the specially selected value of *R* in the form of Eqn (4.26) that determines ρ_{ob}^{E}] can also be obtained using the generalized Boltzmann principle in Leontovich's formulation [14]. The latter is based on the introduction of auxiliary force fields which ensure the reversibility of the object transition from an equilibrium to a quasi-equilibrium state.

4.3 Fluctuation distribution function in Einstein's approach

The simplified expression for the Einstein distribution function (4.22), commonly used in the scientific literature, can be obtained having regard to the *quasi-equilibrium* condition — that is, the condition of smallness of fluctuations $\Delta P_k^{\rm E}$. Expanding the difference ΔS with respect to these

³⁴Arguments in favor of such a heuristic procedure can be derived, for example, from the principle of maximum entropy [37] as well as from the general methods of mathematical statistics as applied to physical measurements (for more details see Section 6.2).

quantities up to the first nonvanishing term in the exponent in Eqn (4.22), we find (in concise notation, dropping out the superscript 'E' and the matrix indices k, l in the intermediate expressions)

$$\Delta S\{\Delta P\} = \Delta_1 S\{\Delta P\} + \frac{1}{2} \Delta_2 S\{\Delta P\} + \dots, \qquad (4.32)$$

where

$$\Delta_1 S\{\Delta P\} = \frac{\partial S\{P\}}{\partial P} \bigg|_{P=\overline{P}} (\Delta P) = \sum_k F_k \Delta P_k , \qquad (4.33)$$

$$\Delta_2 S\{\Delta P\} = \frac{\partial^2 S\{P\}}{\partial P^2} \bigg|_{P=\overline{P}} (\Delta P \Delta P) = \sum_{kl} \sigma_{kl} \Delta P_k \Delta P_l . (4.34)$$

Obviously, the term linear in ΔP in Eqn (4.33) is completely balanced out by the respective term in the exponent in Eqn (4.22), while the term bilinear in ΔP in Eqn (4.34) is negatively defined by virtue of the condition of maximum (even though not absolute but conditional) entropy $S\{P_i\}$ at the state of equilibrium.

Using relations (4.21), (4.32)-(4.34), we obtain three equivalent representations of the Einstein distribution function in the lowest approximation:

$$\rho^{\mathrm{E}}\{\Delta P_i\} = A \exp\left[-\frac{1}{2}\sum_{kl}(-\sigma_{kl})\,\Delta P_k\,\Delta P_l\right],\qquad(4.35\mathrm{a})$$

$$\rho^{\mathrm{E}}\{\Delta F_{i}, \Delta P_{i}\} = B \exp\left[\frac{1}{2}\sum_{k} \Delta F_{k} \Delta P_{k}\right], \qquad (4.35b)$$

$$\rho^{\mathrm{E}}\{\Delta F_i\} = C \exp\left[-\frac{1}{2}\sum_{kl}\varphi_{kl}\Delta F_k\Delta F_l\right].$$
(4.35c)

Here A, B and C are constants found from the normalization conditions by integrating the functions (4.35) over the entire 'space of events' (these constants are finite because the Gaussian exponent is a rapidly decreasing function).

All three forms of the distribution function (4.35) are *normal* or *Gaussian* with respect to the corresponding variables; the choice of the particular representation is usually dictated by the conditions of the problem (see Section 5). In particular, from Eqns (4.35a) and (4.35c) it follows that

$$\overline{\Delta F_k^{\rm E}} = \overline{\Delta P_k^{\rm E}} = 0 \,, \tag{4.36}$$

i.e. the mean values of fluctuations of both E-variables and Gvariables go to zero. At the same time, the bilinear correlation functions of fluctuations of extensive and intensive Evariables are, respectively, as follows

$$\overline{\Delta P_k^{\rm E} \, \Delta P_l^{\rm E}} \equiv \overline{\Delta P_k \, \Delta P_l}^{\rm E} \equiv (-\hat{\sigma}^{-1})_{kl}, \qquad (4.37)$$

$$\overline{\Delta F_k^{\rm E} \Delta F_l^{\rm E}} \equiv \overline{\Delta F_k \Delta F_l}^{\rm E} \equiv (\hat{\varphi}^{-1})_{kl}.$$
(4.38)

If required, expressions (4.37) and (4.38) with due account for relations (4.21) can be used for finding the 'mixed' correlation functions of the form $\Delta F_k^{\rm E} \Delta P_l^{\rm E}$.

It is important that, with due account for equality (4.17), the correlation function (4.37) in Einstein's approach coincides with its counterpart (4.12) in the Gibbs approach:

$$\overline{\Delta P_k \,\Delta P_l}^{\rm E} = \overline{\Delta P_k \,\Delta P_l}^{\rm G} \,. \tag{4.39}$$

Strictly speaking, there are no *a priori* reasons for such a coincidence, because these quantities have a very different physical meaning and are defined in different 'spaces of events'. We believe, however, that it is this coincidence that gives the solid physical sense to the concept of fluctuations in the Gibbs approach. Otherwise they would have been *unobservable* entities, because a macroscopic observer has no 'access' to the phase space where the fluctuations of random dynamic quantities take place according to the Gibbs approach.

In this respect Einstein's approach is closer to physical reality, because according to definition (4.20) the correlation function (4.37) involves fluctuations of random extensive thermodynamic quantities. On top of that, Einstein's approach is also more realistic because it involves a nonzero correlation function of fluctuations of intensive thermodynamic quantities (4.38), which is totally absent in the Gibbs approach. In this way, Einstein's approach 'gives equal rights' to thermodynamic quantities differently from the Gibbs approach, they are not tied to the selection of the 'appropriate' ensemble, and may both fluctuate simultaneously.

5. Quasi-equilibrium pressure fluctuations in Einstein's approach

For the calculation of correlations and variances (including the pressure fluctuations of concern) in the framework of Einstein's approach, according to expressions (4.37) and (4.38), we first of all need to go over from the Gibbs (random dynamic) G-variables $P_k^G(\Gamma)$ and fixed thermodynamic parameters F_k^G = const to Einstein's (random thermodynamic) E-variables P_k^E and F_k^E . It is essential that for the quantities P_k this procedure, according to Eqn (4.22), is defined ³⁵ only for the thermodynamically conjugated pairs of quantities that enter the phase index (4.2) [and, therefore, the distribution function (4.6)]. As far as the quantities F_k are concerned, the same procedure for them is expressed by formula (4.21).

In some cases (in particular, in the analysis of PFs) there is a need for extending the basic set of G-variables (for example, in the transition from the isochoric to the isobaric regime). This, however, runs into a technical difficulty, which prevents a straightforward application of expressions (4.12), (4.37) and (4.38). This difficulty is related to the fact that variables $\{F_k\}$ (contrary to the assumption made in Section 4.2) are not independent, and so the Massieu–Planck function $\Phi\{F_i\}$ loses its 'generating' property (4.4), whereas the similar property (4.5) for the entropy $S\{P_i\}$ remains in place.

5.1 Fluctuations and correlation functions. Transition from G-variables to E-variables

Concrete calculations of correlation functions, defined by expressions (4.12) for G-variables or expressions (4.37) and (4.38) for E-variables, call for the transition from quantities $\{F_k\}$ to new, truly independent intensive quantities $\{f_k\}$ which are defined below. In so doing the formal structure of

³⁵ For example, the attempt to accomplish such a transition by 'erasing' the argument Γ (and hence actually performing averaging) directly in the definition of pressure $P(\Gamma)$ in Eqn (2.9) leads to the generally incorrect result $\overline{P} = -\partial \overline{H}/\partial V$ which, in particular, gives $\overline{P} \equiv 0$ for an ideal gas when \overline{H} does not depend on V.

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the theory then becomes much more complicated than the theory presented in Sections 4.1 and 4.3. In particular, in place of two matrices $\hat{\varphi}$ and $\hat{\sigma}$, defined by equations (4.13) and (4.16), one has to use six matrices $\hat{\sigma}$, $\hat{\phi}$, $\hat{\lambda}$, $\hat{\mu}$, $\hat{\pi}$, and $\hat{\psi}$, of which only $\hat{\sigma}$ retains its former definition (4.16).

Matrices $\hat{\lambda}$ and $\hat{\mu}$ (generally nonsymmetrical) define, like Eqn (4.21), the new linkages between fluctuations of extensive and intensive E-variables:

$$\Delta P_k^{\rm E} = -\sum_l \lambda_{kl} \Delta f_l^{\rm E}, \quad \Delta F_k^{\rm E} = -\sum_l \mu_{kl} \Delta f_l^{\rm E}. \tag{5.1}$$

Matrices $\hat{\pi}$ and $-\hat{\sigma}$ define the correlation functions of extensive G-variables and E-variables, respectively:

$$\overline{\Delta P_k \,\Delta P_l}^{\rm G} = \pi_{kl} \,, \quad \overline{\Delta P_k \,\Delta P_l}^{\rm E} = (-\hat{\sigma}^{-1})_{kl} \,. \tag{5.2}$$

Both matrices are symmetrical, positive-definite and satisfy the condition $(-\hat{\sigma})\hat{\pi} = 1$, so that the equality (4.39) still holds for the correlation functions (5.2).

Correlation functions involving fluctuations of the intensive G-variables are zero by definition:

$$\overline{\Delta f_k \, \Delta P_l}^{\mathbf{G}} = \overline{\Delta f_k \, \Delta f_l}^{\mathbf{G}} \equiv 0 \,, \tag{5.3}$$

whereas for the E-variables we have

$$\overline{\Delta f_k \,\Delta f_l}^{\mathbf{E}} = (\hat{\psi}^{-1})_{kl} \,. \tag{5.4}$$

Mixed correlation functions of the form $\overline{\Delta f_k \Delta P_l}^{\text{E}}$ can be further obtained by using expressions (5.2) and (5.3) and linkages (5.1). Finally, the symmetrical and positive-definite matrix $\hat{\phi}$ is the analogue of the matrix $\hat{\phi}$ from Eqn (4.13) [but, of course, $\hat{\phi} \neq \hat{\phi}$]:

$$\tilde{\varphi}_{kl} = \tilde{\varphi}_{lk} = -\frac{\partial \tilde{\varphi}_k}{\partial f_l}, \quad \tilde{\varphi}_k \equiv -\frac{\partial \Phi\{f_i\}}{\partial f_k}.$$
(5.5)

This matrix is used in the definitions of matrices $\hat{\lambda}, \hat{\pi}$, and $\hat{\psi}$.

The general form of the above matrices can be deduced from the following considerations. In all Gibbs ensembles used as the initial ensembles, the 'leading' dynamic quantity $P_1(\Gamma)$ is the energy $\mathcal{H}(\Gamma)$, whence it follows that $F_1 = \beta$. For all other quantities $P_k(\Gamma)$ with $k \ge 2$ — for example, the generalized force A_i (with the exception of pressure P), volume V, number of particles N, etc. — the thermodynamically conjugated parameters F_k have the form $F_k = \beta f_k$. Here f_k is the generalized coordinate (external field a, pressure P, chemical potential μ , etc.). Obviously, in all these cases the truly independent quantities are β and $\{f_k\}$ ($k \ge 2$), so that $F_1 = f_1$, $F_k = f_1 f_k$.

For the sake of simplicity, we confine ourselves to the case of two variables (without specifying f_2 so far):

$$F_1 = f_1 = \beta, \quad F_2 = f_1 f_2.$$

Then the Gibbs distribution function, according to Eqn (4.1), becomes

$$\rho^{\rm G}(\Gamma; f_1, f_2) = \exp\{-\Phi(f_1, f_2) - f_1[P_1(\Gamma) + f_2 P_2(\Gamma)]\},$$
(5.6)

while the Massieu–Planck function $\Phi(f_1, f_2)$ loses its 'generating' property (4.4) only with respect to the quantity

 \overline{P}_1 , but not to \overline{P}_2 . Indeed,

$$-\frac{\partial \Phi}{\partial F_1} = \tilde{\varphi}_1 = \overline{\tilde{P}}_1, \quad \widetilde{P}_1(\Gamma) = P_1(\Gamma) + f_2 P_2(\Gamma),$$

whereas

$$-\frac{\partial\Phi}{\partial F_2} = -\frac{1}{f_1}\,\tilde{\varphi}_2 = \overline{P}_2\,,$$

so that

$$\overline{P}_1 = \tilde{\varphi}_1 - \frac{f_2}{f_1} \tilde{\varphi}_2$$

Differentiating the normalization condition for the function (5.6) with respect to f_1 and f_2 (see Sections 2.4 and 4.1), it is easy to find the first of the expressions (5.1), whose structure is much more complicated than that of Eqn (4.12):

$$\pi_{kl} = \pi_{lk} , \ \ \lambda_{kl}
eq \lambda_{lk} , \ \ \lambda_{kl} \equiv - rac{\partial P_k}{\partial f_l} ,$$

with

$$\pi_{11} = \lambda_{11} - f_2 \lambda_{21} + \frac{f_2^2}{f_1} \lambda_{22} , \quad \pi_{22} = \frac{1}{f_1} \lambda_{22}$$
$$\pi_{12} = \frac{1}{f_1} \lambda_{12}, \quad \pi_{21} = \lambda_{21} - \frac{f_2}{f_1} \lambda_{22} .$$

In turn one has

$$\begin{split} \lambda_{11} &= \tilde{\varphi}_{11} - \frac{f_2}{f_1} \chi_{12} \,, \quad \lambda_{22} = \frac{1}{f_1} \tilde{\varphi}_{22} \,, \quad \chi_{12} \equiv \tilde{\varphi}_{12} - \frac{1}{f_1} \tilde{\varphi}_2 \,, \\ \lambda_{21} &= \frac{1}{f_1} \chi_{12} \,, \quad \lambda_{12} = \chi_{12} - \frac{f_2}{f_1} \tilde{\varphi}_{22} \,. \end{split}$$

Transition from the Gibbs distribution function (5.6) to the Einstein distribution function occurs in exactly the same way as presented in Section 4. In so doing the entropy $S(\overline{P}_1, \overline{P}_2)$ is still defined by Eqn (4.3) and retains its 'generating' properties (4.5) with respect to both variables F_1 and F_2 , as well as f_1 (but not f_2):

$$\frac{\partial S}{\partial \overline{P}_1} = F_1 = f_1, \quad \frac{\partial S}{\partial \overline{P}_2} = F_2 = f_1 f_2.$$
(5.7)

In Eqn (5.7) it is assumed that the intensive parameters $\{f_k\}$ [and thus the Massieu–Planck function $\Phi(f_1, f_2)$] are expressed as functions of the extensive parameters $\{\overline{P}_k\}$, so that the definitions (4.3) and (4.5) remain in force.

As a result, we again come to the Einstein distribution function in the form (4.35a), and hence to the expression (4.37) for the correlation function of fluctuations of thermodynamic E-variables. One can prove its exact similarity to the correlation function (5.2) of fluctuations of dynamic G-variables by again using the 'orthogonality condition' (4.18) and taking into account the nonlinear structure of the second relation in Eqn (5.5), when differentiating F_2 with respect to \overline{P}_1 and \overline{P}_2 . Then, using the first relation in Eqn (4.21), we come again to the Einstein distribution function in the form (4.35b).

However, the Einstein distribution function for fluctuations of the intensive E-variables, $\Delta f_k^{\rm E}$, is now different from function (4.35c), because in place of relations (4.21) that describe the linkage of fluctuations $\Delta P_k^{\rm E}$ and $\Delta F_k^{\rm E}$ we now must use Eqn (5.1). Substituting these expressions into Eqn (4.35b), defining the matrix $\hat{\psi}$ as $\psi_{lm} = \sum_k \mu_{kl} \lambda_{km}$, and taking into account that $\mu_{11} = 1$, $\mu_{12} = 0$, $\mu_{21} = f_2$, and $\mu_{22} = f_1$, we find

$$\rho^{\mathrm{E}}\{\Delta f_i\} = C \exp\left[-\frac{1}{2}\sum_{kl}\psi_{kl}\,\Delta f_k\,\Delta f_l\right].$$
(5.8)

Here, the symmetrical and positive-definite matrix $\hat{\psi}$ has a simple form that almost coincides with the form of matrix $\hat{\phi}$:

$$\psi_{11} = \tilde{\varphi}_{11}, \quad \psi_{12} = \psi_{21} = \chi_{12}, \quad \psi_{22} = \tilde{\varphi}_{22}.$$

From Eqn (5.8) directly follows expression (5.4).

Concrete calculations of correlation functions (5.2) and (5.4) depend on the selection of the initial independent G-variables (in this case, the conjugate pair of $P_2(\Gamma)$ and f_2); appropriate examples are considered in Section 5.2.

5.2 Statistical method for computing PFs. Solution of the Einstein problem

Let us consider two examples of calculation of G- and Evariable fluctuations (including PFs) for the classical case of an ideal gas, when the explicit form of functions $\Phi\{f_i\}$ and $S\{\overline{P}_i\}$ can be found. Such a calculation can aptly be called *statistical*, to distinguish it from the commonly used *thermodynamic* calculation (see Section 5.3); to the best of our knowledge, such a method is used in the context of Einstein's approach for the first time ever.

Isothermal-isochoric situation. In the Gibbs approach, the isothermal-isochoric situation is characterized by the pair of conjugate G-variables:

$$P_1^{\mathbf{G}}(\Gamma) = \mathcal{H}_V(\Gamma), \quad F_1^{\mathbf{G}} = f_1 = \beta, \qquad (5.9)$$

which enter the phase index. Differently from F_1 , the parameter V = const is dynamic and implicitly enters $P_1^G(\Gamma)$. The conjugate dynamic quantity [pressure $P_V(\Gamma)$] is defined by Eqn (2.9), and the conventional transition to E-variables using this pair of quantities is not possible (see footnote 35). For this situation, the initial Gibbs distribution function (5.6) assumes the form (2.17) in the special case a = 0.

For an ideal gas in the nondegenerate regime in both the classical and quantum descriptions, the Massieu–Planck function $\Phi(\beta, V)$ is given by Eqn (3.48) and gives rise to Gibbs' thermodynamics — relations (3.49)–(3.57). Matrices $\hat{\phi}$ and $\hat{\psi}$ become one-dimensional (scalar), so that the fluctuations of E-variables $P_1^{\rm E} = \mathcal{H}$ and $F_1^{\rm E} = \beta$ can easily be found. Indeed, according to Eqn (5.2), we have

$$\overline{\left(\Delta\mathcal{H}\right)^2}^{\rm E} = \overline{\left(\Delta\mathcal{H}\right)^2}^{\rm G} = \tilde{\varphi}_{11} = N \frac{f}{2} \frac{1}{\beta^2} \,. \tag{5.10}$$

Using Eqn (3.53) for $\overline{\mathcal{H}}$, we arrive at

$$[\xi_{\mathcal{H}}^2]^{\rm E} = [\xi_{\mathcal{H}}^2]^{\rm G} = \frac{2}{f} \frac{1}{N}, \qquad (5.11)$$

which naturally coincides with Eqn (3.57).

Similarly, according to relation (5.4), we have

$$\overline{\left(\Delta\beta\right)^2}^{\rm E} = \tilde{\varphi}_{11}^{-1} = \frac{1}{N} \frac{2}{f} \beta^2 \,, \quad \overline{\left(\Delta\beta\right)^2}^{\rm G} \equiv 0 \,.$$

Using the equality $\Delta\beta = -\beta(\Delta T/T)$, one gets

$$\xi_{\beta}^{2}]^{\mathrm{E}} = [\xi_{T}^{2}]^{\mathrm{E}} = \frac{2}{f} \frac{1}{N}.$$
 (5.12a)

Observe that the absolute variances of E-variables β and \mathcal{H} are mutually inverse ³⁶:

$$\overline{\left(\Delta\beta\right)^2}^E \overline{\left(\Delta\mathcal{H}\right)^2}^E = 1, \qquad (5.12b)$$

while their relative variances are equal to each other:

$$\left[\xi_{\beta}^{2}\right]^{\mathrm{E}} = \left[\xi_{\mathcal{H}}^{2}\right]^{\mathrm{E}}.$$
(5.12c)

It is not possible, however, to calculate the fluctuations of volume and pressure according to Einstein's approach in the framework of this isothermal–isochoric situation. To accomplish this, it is necessary to extend the initial set of G-variables, which currently means going over to the isothermal–isobaric situation.

Isothermal-isobaric situation. The required extension of the initial set of variables consists in that the pair of G-variables (5.9) is supplemented with the pair of G-variables

$$P_2^{\rm G}(\Gamma) = V(\Gamma), \quad F_2^{\rm G} = \beta P, \quad f_2 = P,$$
 (5.13)

which permits, according to Eqns (4.22) and (4.21), the transition to E-variables. Then the initial Gibbs distribution function (5.6) becomes

$$\rho^{\rm G}(\Gamma;\beta,P) = \exp\left\{-\Phi(\beta,P) - \beta\left[\mathcal{H}(\Gamma) + PV(\Gamma)\right]\right\}, (5.14)$$

so that the derivative

$$-\frac{\partial\Phi}{\partial\beta} = \overline{\mathcal{H}} + P\overline{V} = \overline{\mathcal{H}}$$

defines the mean enthalpy \overline{H} , while the derivative

$$-\frac{1}{\beta} \frac{\partial \Phi}{\partial P} = \overline{V} \tag{5.15}$$

gives the mean volume. The mean energy $\overline{\mathcal{H}}$ is determined by

$$\overline{\mathcal{H}} = \overline{H} - P\overline{V} = -\frac{\partial\Phi}{\partial\beta} + \frac{P}{\beta}\frac{\partial\Phi}{\partial P}.$$
(5.16)

The statistical integral $\mathcal{Z}(\beta, P)$ for the isothermal-isobaric situation is linked with $\mathcal{Z}(\beta, V)$ for the isothermal-isochoric situation by the Laplace transformation (see, for example, Ref. [14]):

$$\mathcal{Z}(\beta, P) = \int_0^\infty dV \exp(-\beta PV) \,\mathcal{Z}(\beta, V) \,. \tag{5.17}$$

Using expressions (3.46) and (3.47) in Eqn (5.17), for the case of an ideal gas we have

$$\mathcal{Z}(\beta, P) = \beta^{-N(f/2+1)} P^{-N}(bN!)$$

³⁶ Expression (5.12b) is an example of *uncertainty relations* in statistical thermodynamics (see, for instance, Refs [45–47]).

Hence, up to some immaterial constants, we get the Massieu–Planck function in the form

$$\Phi(\beta, P) = -N\left[\left(\frac{f}{2} + 1\right)\ln\beta + \ln P\right]$$
(5.18)

and then, using definition (4.3), the entropy

$$S(\overline{H},\overline{V}) = N\left[\frac{f}{2}\ln\overline{\mathcal{H}} + \ln\overline{V}\right].$$
(5.19)

In going over from Eqn (5.18) to Eqn (5.19) we used the fact that, according to Eqns (5.15) and (5.16), the thermal and caloric TDEOS are as follows

$$\overline{V} = \frac{N}{\beta P}, \quad \overline{\mathcal{H}} = N \frac{f}{2} \frac{1}{\beta}.$$
 (5.20)

Then the intensive thermodynamic parameters entering Eqn (5.18) can be expressed in terms of the extensive variables as follows

$$P = \frac{2}{f} \frac{\overline{\mathcal{H}}}{\overline{\mathcal{V}}}, \quad \beta = N \frac{f}{2} \frac{1}{\overline{\mathcal{H}}}.$$
(5.21)

The matrices $\hat{\phi}$ and $\hat{\sigma}$ (diagonal in this case) required for the calculation of the correlation functions (5.2) and (5.4) are written as

$$\begin{split} \tilde{\varphi}_{12} &= \tilde{\varphi}_{21} = 0 \,, \quad \tilde{\varphi}_{11} = N \left(\frac{f}{2} + 1 \right) \frac{1}{\beta^2} \,, \quad \tilde{\varphi}_{22} = N \frac{1}{P^2} \,, \\ \sigma_{12} &= \sigma_{21} = 0 \,, \quad \sigma_{11} = -N \, \frac{f}{2} \, \frac{1}{\mathcal{H}^2} \,, \quad \sigma_{22} = -N \, \frac{1}{\mathcal{V}^2} \,. \end{split}$$

According to functions (5.2), the quantities σ_{kl} suffice for finding the correlation functions of the extensive E- or G-variables. In particular, by virtue of the property $\sigma_{12} = \sigma_{21} = 0$, for the correlation function of fluctuations of energy and volume we have

$$\overline{\Delta \mathcal{H} \Delta V}^{\rm G} = \overline{\Delta \mathcal{H} \Delta V}^{\rm E} = 0$$

Moreover, given the form of the Einstein distribution function (4.35a), the quantities \mathcal{H}^{E} and V^{E} are not only noncorrelated but also completely independent statistically, because of the equality

$$\rho^{\mathrm{E}}\{\Delta\mathcal{H}, \Delta V\} = \rho^{\mathrm{E}}\{\Delta\mathcal{H}\}\,\rho^{\mathrm{E}}\{\Delta V\}\,,\tag{5.22}$$

where

$$\rho^{\mathrm{E}}\{\Delta\mathcal{H}\} = A_1 \exp\left[\sigma_{11}(\Delta\mathcal{H}^{\mathrm{E}})^2\right],$$
$$\rho^{\mathrm{E}}\{\Delta V\} = A_2 \exp\left[\sigma_{22}(\Delta V^{\mathrm{E}})^2\right].$$

Observe that the noncorrelated E-variables, by contrast to G-variables, are not β and P but rather β and V, because, as is easily proved, the following relations take place:

$$\overline{\Delta P \Delta \beta}^{\rm E} = -\frac{1}{N} \frac{2}{f}, \quad \overline{\Delta P \Delta V}^{\rm E} = -\frac{1}{\beta}, \quad \overline{\Delta \beta \Delta V}^{\rm E} = 0.$$
(5.23)

The variances (both absolute and relative) of energy are, as before, expressed by Eqns (5.10) and (5.11) obtained earlier

for the isothermal-isochoric situation. The variances of volume (absolute and relative) are given by

$$\overline{(\Delta V)^2}^{\rm E} = \overline{(\Delta V)^2}^{\rm G} = \frac{N}{\beta^2 P^2}, \quad [\xi_V^2]^{\rm E} = [\xi_V^2]^{\rm G} = \frac{1}{N}. \quad (5.24)$$

The situations with variances of the intensive thermodynamic parameters β and *P* in the case of G- and E-variables are entirely different. Indeed, in the Gibbs approach, according to the definition of the isothermal–isobaric ensemble (5.13), these variances are strictly zero:

$$\overline{\left(\Delta\beta\right)^2}^{\rm G} = \overline{\left(\Delta P\right)^2}^{\rm G} = 0 \,.$$

In Einstein's approach, however, for the variances of the inverse temperature β (which exactly coincides with the variance of the temperature *T* itself) and the pressure *P*, we get, according to Eqn (5.4), nonzero expressions. The relative variance of the temperature is given again by Eqn (5.12a), while the variances (absolute and relative) of pressure are written as

$$\overline{(\Delta P)^{2}}^{E} = \hat{\psi}_{22}^{-1} = \frac{1}{N} \left(\frac{2}{f} + 1\right) P^{2},$$
$$[\xi_{P}^{2}]^{E} = \frac{1}{N} \left(\frac{2}{f} + 1\right).$$
(5.25)

As shown in Section 5.3, formulas (5.25) exactly coincide with those obtained by Landau and Lifshitz [7] in the framework of Einstein's approach using the thermodynamic calculating method.

Comparing (5.25) with (3.26), we again come to the difference (3.62) between the results of calculations of PFs in the framework of the Gibbs and Einstein approaches for the case of an ideal gas in the nondegenerate regime.

Solution of the Einstein problem for PFs. As shown in Section 4.2, the descriptions of fluctuations in the approaches of Gibbs and Einstein have, generally speaking, considerably different physical backgrounds. It is not always easy, however, to take into account their influence on the particular calculations, especially in the computations of variances of the intensive thermodynamic parameters (including the pressure).

Nevertheless, in the case of an ideal gas it is possible to identify convincingly the cause of disagreement (3.62), which is neither a mistake nor an accident. As shown below, this difference is a consequence of the feasibility of simultaneous fluctuations of the pair of mutually conjugated thermodynamic parameters (for example, pressure and volume) in Einstein's approach, which is not possible in the Gibbs approach.

To understand the role of volume fluctuations when calculating PFs according to Einstein, one must interpret the thermal equation of state (5.21) not as the relation between the fixed mean values of variables $\overline{\mathcal{H}}$, \overline{V} and the fixed thermodynamic parameter P (as is done in the Gibbs approach to G-variables), but rather as the linkage between the random (and therefore fluctuating) quantities (which is a mark of Einstein's approach to E-variables).

We write the thermal TDEOS for E-variables in the form

$$P = \frac{2}{f} \mathcal{H} V^{-1} \tag{5.26}$$

and note its exact coincidence in form with the corresponding thermal TDEOS (3.44) for G-variables. The distinction lies in the different treatment of the volume V in the two expressions: in Eqn (3.44) it is strictly fixed, while in Eqn (5.26) this quantity can fluctuate (and is therefore characterized by a variance). It is this fundamental difference that causes the deviation (3.62) for PFs, and thus resolves the Einstein problem (in the narrow sense)³⁷.

To be convinced of this, let us calculate PFs (or more precisely, the relative variance ξ_P^2) directly from Eqn (5.26), taking into account that due to equality (5.22) the random quantities \mathcal{H} and V are independent. Then for the relative variance of the product of these quantities we have (see, for example, Ref. [38]) the following relationship

$$\xi_{XY}^2 = \xi_X^2 + \xi_Y^2 + \xi_X^2 \xi_Y^2.$$
(5.27)

In this instance $X = a\mathcal{H}$, a = 2/f, and $Y = V^{-1}$; we must also take into account the condition $\xi_{V^{-1}} = \xi_V$ and the property (3.24).

Since the relative variances of \mathcal{H} and V, according to Eqns (5.11) and (5.24), are proportional to 1/N, then in the lowest order in 1/N we may drop out the last term on the right-hand side of relationship (5.27). Then one finds

$$[\xi_P^2]^{\rm E} = [\xi_{\mathcal{H}}^2]^{\rm E} + [\xi_V^2]^{\rm E} \,. \tag{5.28}$$

Taking into account that, according to Eqns (3.57) and (5.11), the following relation holds for relative variances

$$[\xi_P^2]^{\mathbf{G}} = [\xi_{\mathcal{H}}^2]^{\mathbf{G}} = [\xi_{\mathcal{H}}^2]^{\mathbf{E}},$$
(5.29)

and using Eqn (5.24), we finally find

$$[\xi_P^2]^{\rm E} - [\xi_P^2]^{\rm G} = [\xi_V^2]^{\rm E} = \frac{1}{N}.$$
(5.30)

As ought to be expected, expression (5.30) for the difference in the results for PFs, obtained through the approaches of Gibbs and Einstein, exactly coincides with expression (3.62) derived earlier in a different way.

5.3 Thermodynamic method for computing PFs

In most cases the explicit form of the Massieu–Planck function $\Phi{f_i}$ and/or the entropy $S{\overline{P_i}}$ is not known (for example, for arbitrary nonideal macroscopic systems). Then the calculation of correlations and variances of E-variables is based on a method which (in spite of the express use of the Einstein distribution function) may be naturally referred to as the *thermodynamic* method.

Differently from the statistical method (see Section 5.2), the thermodynamic method is rather phenomenological: it does not provide explicit expressions for the required variances, but only establishes their linkages with other thermodynamic quantities (as a rule, static susceptibilities ³⁸). The latter in turn are assumed to be known, for example, from simulations or experiments. To find such linkages in the case of E-variables, it is expedient to apply the following procedure. We select the Einstein distribution function in the form (4.35b), and carry out transformation (5.1) from variables { F_i } to { f_i } in this function. Then, with

³⁷ A similar situation, related to the distinction between G- and E-variables, is also encountered with other physical quantities. It may be called *Einstein's problem in the broad sense*.

 38 Observe that for fluctuations of G-variables such linkages are established by Eqns (2.41)–(2.43).

due account for the form of matrix $\hat{\mu}$, we get

$$\rho^{\mathrm{E}}(\{\Delta f_i\}, \{\Delta P_i\}) = B \exp\left[\frac{1}{2}\sum_{kl}\mu_{kl}\Delta f_l\Delta P_k\right]$$
$$= B \exp\left[\frac{1}{2}\left[\Delta f_1(\Delta P_1 + f_2\Delta P_2) + f_1\Delta f_2\Delta P_2\right]\right]. \quad (5.31)$$

For the case under consideration, when $f_1 = \beta$, $P_1 = \mathcal{H}$, $f_2 = P$, $P_2 = V$, the main thermodynamic identity gives us

$$\Delta P_1 + f_2 \,\Delta P_2 = \Delta \mathcal{H} + P \,\Delta V \equiv \Delta H = T \,\Delta S \,.$$

Here, ΔH and ΔS are the fluctuations of enthalpy and entropy, respectively.

Now going over from β to $T = 1/k_{\rm B}\beta$, and noting that $\Delta\beta = -\Delta T/k_{\rm B}T^2$, where ΔT is the temperature fluctuation, for $\rho^{\rm E}$ we finally find the expression

$$\rho^{\rm E} = B \exp\left[-\frac{1}{2k_{\rm B}T} \left(\Delta T \Delta S - \Delta P \Delta V\right)\right].$$
 (5.32)

The distribution function for thermodynamic fluctuations in the form (5.32) in the framework of the general Einstein approach was first obtained by Landau and Lifshitz [7] based on the principle of least work (see also Refs [15-17]). Expression (5.32) is the starting point for the thermodynamic method of calculation of any fluctuations, including PFs.

The further procedure of calculation consists in the selection (generally speaking, arbitrary because of equal status of all E-variables) of a pair of variables (for example, P and S, P and V, P and T, etc.) as independent variables, and the transformation of the function $\rho^{\rm E}$ from Eqn (5.32) to the Gaussian form in these variables. Formally this can be accomplished either using the technique of Jacobians [16, 17, 19] or by straightforward calculations [15–17, 22] embracing fluctuations of the dependent variables (in the linear approximation) with subsequent substitution into the exponent in Eqn (5.32). The right choice of truly independent variables leads to mutual compensation of mixed products with respect to their fluctuations. Then the distribution function (5.32), which considerably simplifies the calculations.

The best choice of independent E-variables for our purposes is the pair involving volume V and temperature T, which is reasonable in the light of the last relation in Eqn (5.23). Then one arrives at

$$\Delta S = \left[\frac{\partial S}{\partial T}\right]_{V} \Delta T + \left[\frac{\partial S}{\partial V}\right]_{T} \Delta V, \qquad (5.33)$$

$$\Delta P = \left[\frac{\partial P}{\partial T}\right]_{V} \Delta T + \left[\frac{\partial P}{\partial V}\right]_{T} \Delta V, \qquad (5.34)$$

and according to the Maxwell relation and the definition of heat capacity at constant volume C_V we have

$$\begin{bmatrix} \frac{\partial S}{\partial V} \end{bmatrix}_T = \begin{bmatrix} \frac{\partial P}{\partial T} \end{bmatrix}_V, \quad \begin{bmatrix} \frac{\partial S}{\partial T} \end{bmatrix}_V = \frac{1}{T} \begin{bmatrix} \frac{\partial H}{\partial T} \end{bmatrix}_V = \frac{C_V}{T}.$$
 (5.35)

It is essential that here and further in the spirit of Einstein's approach all thermodynamic derivatives are assumed to be 'equilibrium' — that is, in their calculations one has to neglect fluctuations and set

$$T \approx \overline{T}, \quad V \approx \overline{V}, \quad P \approx \overline{P}.$$
 (5.36)

Using the linkages (5.35), it is easy to see that the mixed products of the form $\Delta T \Delta V$ entering the exponent in formula (5.32) cancel out ³⁹, so that Eqn (5.32) only contains terms quadratic with respect to ΔT and ΔV . Hence it follows that

$$\rho^{\mathrm{E}}(\Delta T, \Delta V) = \rho^{\mathrm{E}}(\Delta T) \,\rho^{\mathrm{E}}(\Delta V) \,, \tag{5.37a}$$

where

$$\rho^{\mathrm{E}}(\Delta T) = A_T \exp\left\{-\frac{C_V}{2k_{\mathrm{B}}T^2}(\Delta T)^2\right\},\qquad(5.37b)$$

$$\rho^{\rm E}(\Delta V) = A_V \exp\left\{\frac{1}{2k_{\rm B}T} \left[\frac{\partial P}{\partial V}\right]_T (\Delta V)^2\right\},\qquad(5.37c)$$

so that the random variables T, V are not only noncorrelated, but completely statistically independent. Observe that in this case the 'nondiagonal' correlation function $\overline{\Delta V \Delta T}^{\rm E}$ vanishes not only for the ideal gas, as in relations (5.23), but also for a more general macrosystem (of course, as long as the Gaussian approximation is valid).

For the 'diagonal' correlation functions (absolute variances), according to Eqns (5.37b) and (5.37c), we have

$$\overline{\left(\Delta T\right)^2}^{\rm E} = \frac{k_B T^2}{C_V}, \quad \overline{\left(\Delta V^2\right)}^{\rm E} = k_B T V \varkappa_T, \qquad (5.38a)$$

where $\varkappa_T = -(1/V)[\partial V/\partial P]_T$ is the isothermal compressibility. It is not difficult to calculate other correlation functions as well, for example,

$$\overline{\Delta P \Delta V}^{\mathrm{E}} = \left[\frac{\partial P}{\partial T}\right]_{V} \overline{\Delta T \Delta V}^{\mathrm{E}} + \left[\frac{\partial P}{\partial V}\right]_{T} \overline{(\Delta V^{2})}^{\mathrm{E}} = -k_{\mathrm{B}}T,$$

which again coincides with the second relation in Eqn (5.23) for an ideal gas.

Of most interest in the context of this paper is the pressure fluctuation or the absolute pressure dispersion, for which we readily find

$$\overline{(\Delta P)^{2}}^{E} = \left[\frac{\partial P}{\partial T}\right]_{V}^{2} \overline{(\Delta T)^{2}}^{E} + \left[\frac{\partial P}{\partial V}\right]_{T}^{2} \overline{(\Delta V)^{2}}^{E}$$
$$= \left[\frac{\partial P}{\partial T}\right]_{V}^{2} \frac{k_{B}T^{2}}{C_{V}} - \left[\frac{\partial P}{\partial V}\right]_{T} k_{B}T.$$
(5.38b)

Now we take into account the linkage between the thermal pressure coefficient $[\partial P/\partial T]_V$ and the isothermal compressibility $[\partial P/\partial V]_T$ (the Mayer relation):

$$\left[\frac{\partial P}{\partial T}\right]_{V}^{2} = -\frac{C_{P} - C_{V}}{T} \left[\frac{\partial P}{\partial V}\right]_{T},$$

where C_P and C_V are the heat capacities at constant pressure and constant volume, respectively. Using the Poisson coefficient $\gamma = C_P/C_V > 1$, we finally come to the result of Landau and Lifshitz [7] for PFs — relations (1.7) and (1.8) which are different from relations (1.2)–(1.4), which gives rise to the Einstein problem for PFs.

Ideal gas: nondegenerate regime, classical description. Using the values of thermodynamic derivatives (3.50), (3.54) and (3.49) for the respective quantities in Eqn (5.38) as well as in Eqns (1.7) and (1.8), it is easy to come to the same expressions for the relative temperature variances (5.12), volume variances (5.24) and pressure variances (5.25) that

were obtained in Section 5.2 by the statistical method [in the latter case we have noted that the value of γ for an ideal gas is given by expression (3.59)].

It should be well to emphasize that the straightforward and physically transparent expression (5.28) for PFs in the case of an ideal gas can also be obtained within the framework of the thermodynamic approach. This does not require carrying out all the cumbersome calculations that lead first to the general formula in the form (1.7). It will suffice to set both the thermodynamic derivatives in the initial equation (5.34) for the pressure fluctuation ΔP equal to their values (3.50) and (3.51) for an ideal gas. Then we get

$$\Delta P = \frac{Nk_{\rm B}}{V} \left(\Delta T - \frac{T}{V} \Delta V \right). \tag{5.39}$$

Raising both sides of equality (5.39) to the second power and averaging, we find

$$\overline{(\Delta P)^2} = \left(\frac{Nk_{\rm B}}{V}\right)^2 \left[\overline{(\Delta T)^2} + \left(\frac{T}{V}\right)^2 \overline{(\Delta V)^2} - 2 \frac{T}{V} \overline{\Delta T \Delta V}\right].$$

Then, using the property (5.37a), one gets

$$\overline{\left(\Delta P\right)^2} = \left(\frac{Nk_{\rm B}T}{V}\right)^2 \left[\frac{\overline{\left(\Delta T\right)^2}}{T^2} + \frac{\overline{\left(\Delta V\right)^2}}{V^2}\right]$$

and accounting for the thermal equation of state (3.49) one obtains the final result

$$\left[\xi_{P}^{2}\right]^{E} = \left[\xi_{T}^{2}\right]^{E} + \left[\xi_{V}^{2}\right]^{E}, \qquad (5.40)$$

which exactly coincides with expression (5.28) worked out by the above-considered statistical method; we only need to allow for the coincidence between the relative variances of temperature and energy in Einstein's approach, ensured by Eqns (5.12a) and (5.12c). The physical meaning of Eqn (5.40) and its linkage with the expression for $[\xi_P^2]^G$ were discussed in Section 5.2.

Ideal gas: nondegenerate regime, inclusion of quantum exchange corrections. The thermodynamic calculating method allows for a relatively simple introduction of corrections to the variances of thermodynamic variables (including pressure fluctuations) according to Einstein, which arise when the temperature of gas *T* is lowered and/or the volume *V* is decreased. Then the condition $T \ge T_0(V)$ is replaced by a less stringent condition $T \ge T_0(V)$, where $T_0(V) = 2^{2/3} \pi (\hbar^2/mk_B) (N/V)^{2/3}$ is the quantum degeneracy temperature of an ideal gas. Obviously, the gas remains in the nondegenerate regime, but its purely classical description becomes not quite adequate, and one has to include the quantum exchange corrections. With this purpose the thermodynamic quantities can be represented as expansions in powers of $T_0(V)/T$ (see, for example, Refs [7, 17, 21, 26]).

Retaining only the lowest correction, we have the following expressions for the internal energy, the heat capacity at constant volume, and the pressure:

$$E_{\rm Q}(T,V) = E_{\rm C}(T) \left[1 \mp \frac{1}{4} \,\varepsilon(T,V) \right], \qquad (5.41a)$$

$$C_V^{\mathbf{Q}}(T,V) = C_V^{\mathbf{C}} \left[1 \pm \frac{1}{8} \,\varepsilon(T,V) \right], \qquad (5.41b)$$

$$P_{\rm Q}(T,V) = \frac{2E_{\rm Q}(T,V)}{3V} = P_{\rm C}(T,V) \left[1 \mp \frac{1}{4} \,\varepsilon(T,V) \right].$$
(5.41c)

 $^{^{39}}$ A similar property is associated with the selection of the pair of independent variables *P* and *S*, but not *P* and *T* or *P* and *V*.

The upper sign in these formulas corresponds to a Bose gas, and the lower sign to a Fermi gas; the indices Q and C mark quantum and classical quantities, respectively. Then the main thermodynamic parameters in the classical approximation are given by the expressions

$$E_{\rm C}(T) = C_V^{\rm C} T, \quad C_V^{\rm C} = N \frac{3}{2} k_{\rm B}, \quad P_{\rm C}(T, V) = \frac{2}{3V} E_{\rm C}(T),$$

and the quantum corrections are taken into account in the linear approximation with respect to the small parameter

$$\varepsilon(T, V) \equiv \left(\frac{T_0(V)}{T}\right)^{3/2} \ll 1, \quad \frac{\partial \varepsilon}{\partial T} = -\frac{3}{2} \frac{\varepsilon}{T}, \quad \frac{\partial \varepsilon}{\partial V} = -\frac{\varepsilon}{V}.$$

Using the thermal equation of state (5.41c), it is easy to find (dropping for compactness the arguments T, V) the quantum exchange corrections to the thermodynamic derivatives:

$$\frac{\partial P_{\rm Q}}{\partial V} = -\frac{P_{\rm Q}}{V} \left(1 \mp \frac{1}{4} \,\varepsilon \right), \quad \frac{\partial P_{\rm Q}}{\partial T} = \frac{P_{\rm Q}}{T} \left(1 \pm \frac{3}{8} \,\varepsilon \right). \quad (5.41d)$$

Further, in accordance with the general expressions (5.38a), it is not difficult to calculate the quantum exchange corrections to the variances of temperature and volume:

$$\begin{bmatrix} \xi_T^2 \end{bmatrix}_{\mathbf{Q}} = \begin{bmatrix} \xi_T^2 \end{bmatrix}_{\mathbf{C}} \left(1 \mp \frac{1}{8} \varepsilon \right), \quad \begin{bmatrix} \xi_V^2 \end{bmatrix}_{\mathbf{Q}} = \begin{bmatrix} \xi_V^2 \end{bmatrix}_{\mathbf{C}} \left(1 \pm \frac{1}{2} \varepsilon \right).$$
(5.42a)

Substituting these corrections into Eqn (5.38b) for PFs, and accounting for Eqns (5.41d), (5.28) as well as (5.12a) and (5.12c), we finally get

$$\begin{bmatrix} \xi_{P}^{2} \end{bmatrix}_{Q} = \begin{bmatrix} \xi_{P}^{2} \end{bmatrix}_{C} \pm \frac{5}{8} \varepsilon(T, V) \begin{bmatrix} \xi_{T}^{2} \end{bmatrix}_{C},$$
$$\begin{bmatrix} \xi_{P}^{2} \end{bmatrix}_{C} = \begin{bmatrix} \xi_{T}^{2} \end{bmatrix}_{C} + \begin{bmatrix} \xi_{V}^{2} \end{bmatrix}_{C}.$$
(5.42b)

Expression (5.42b) indicates that in the range of temperatures *T* and/or densities N/V, when the quantum properties of microparticles are brought into play in the dynamic description of the macrosystem, the PFs receive an additional (as compared with the classical domain) contribution determined by the temperature fluctuations ⁴⁰ (positive for Bose particles, and negative for Fermi particles).

Obviously, it is possible to include corrections of higher order in ε , as well as corrections for nonideality of the gas — for example, when the thermal equation of state is of the van der Waals type, or of a more general virial type.

6. Conclusions

6.1 The main results

In conclusion, let us draw a summary of our discussion. First of all we want to emphasize the fact that we have given the solution of two known problems in the theory of thermodynamic fluctuations: the Gibbs problem and the Einstein problem for pressure fluctuations (PFs). Comparative analysis of the Gibbs and Einstein approaches to the description of thermodynamic fluctuations on the whole allowed us to obtain several important results, which include the following:

⁴⁰ Note that the volume fluctuations in the linear approximation in ε do not contribute to PFs.

• Within the framework of the Gibbs approach, we have for the first time given (Section 2) a consistent formulation of pressure and compressibility as quasi-dynamic quantities that characterize a macrosystem of finite volume. In doing this we used the analogy with the quasi-mean quantities introduced by Bogolyubov for describing the degenerate states of macrosystems in thermal equilibrium. In the case of pressure and compressibility, the role of the external 'source' that removes spatial degeneration is played by the singular potential of the 'walls' that confine the macrosystem.

• On the basis of these definitions we developed (Section 3) the extension of the Bogolyubov–Zubarev and Hellmann–Feynman theorems, which connect the general expression for the pressure with the specific form of the Hamiltonian function or the Hamiltonian of the macrosystem (with due account for the boundary conditions in the latter case). The generalization consists in expressing a similar linkage for compressibility, which logically completes the approach of Gibbs and gives the solution of the Gibbs problem — a consistent calculation of PFs.

• In the framework of Einstein's approach (Section 5) we proposed a statistical calculating method for correlation functions of fluctuations of the extensive and intensive thermodynamic parameters. For the extensive parameters, the corresponding expressions coincide with those in the Gibbs approach, while the expressions for the intensive parameters are essentially distinctive because of the conceptual difference between the two approaches. We showed that the proposed statistical method is equivalent to the conventional thermodynamic method of Landau and Lifshitz, but is more convenient in those cases when the explicit form of the entropy or the Massieu – Planck function of the macroscopic system is known.

• Treating all the thermodynamic parameters as random variables in the space of macroparameters in the framework of Einstein's approach, we propose (Section 5) a simple method for establishing the linkage between the variances of macroparameters in the thermodynamic equation of state. This method is especially efficient when such parameters are statistically independent. In particular, it gives a simple solution of Einstein's problem for PFs of an ideal gas in the nondegenerate regime in both the classical description and the description with inclusion of the lowest quantum exchange corrections. The proposed method allows skipping the cumbersome intermediate thermodynamic calculations which are required in the case of an arbitrary macrosystem.

The most important result of our analysis relates to the establishment (Section 4) of both the conceptual distinction and the natural affiliation between the two qualitatively different methods of probabilistic description of one and the same macrosystem — the Gibbs and Einstein approaches as a whole.

The Gibbs approach or *statistical mechanics* paves a way to a 'rigid' averaged *microscopic description*, which does not allow for simultaneous fluctuations of the two thermodynamically conjugated parameters (for example, internal energy and temperature, or pressure and volume) in the context of one and the same equilibrium ensemble.

Einstein's approach or *statistical thermodynamics* from the start introduces a probabilistic *macroscopic description* and does not rely on any microscopic description (dynamic 'prototypes' which act as some kind of 'hidden parameters'). In comparison with the Gibbs approach, the approach of Einstein is less rigid because it allows for simultaneous fluctuations of both thermodynamically conjugated quantities in the pair.

Given such considerable conceptual and computing differences between the approaches of Gibbs and Einstein, there initially seemed little chance of establishing a 'genetic linkage' between them. However, our results (Section 4) indicate that the Einstein distribution function can formally be derived from the Gibbs distribution function by the following simple heuristic procedure.

The extensive dynamic quantities that determine the Gibbs distribution function remain random but are 'detached' from the microscopic phase space and are further considered in the space of thermodynamic macroparameters. The intensive thermodynamic quantities or macroparameters, conjugated with the extensive quantities and strictly fixed in the Gibbs approach, must now be stochastized, i.e. also regarded as random variables.

The proposed method of transition 'from Gibbs to Einstein' can be aptly called statistical. It is important that its result for the Einstein distribution function exactly coincides with the result obtained by the traditional 'thermodynamic' method, based on the Boltzmann principle or the equivalent principle of least work used by Landau and Lifshitz.

The consistent treatment of the Gibbs and Einstein approaches reveals their relationship and, in a certain sense, applicability limits. In particular, the Gibbs approach is more efficient for calculating the mean values of physical quantities characterizing a macrosystem at thermal equilibrium, whereas Einstein's approach is preferred for describing the states of macrosystems near thermal equilibrium; moreover, the Einstein approach can be used for refining the very concept of thermal equilibrium.

The proposed procedures of 'macroscopization' of the extensive physical quantities and 'stochastization' of the intensive thermodynamic parameters, which play the key role in the transition 'from Gibbs to Einstein', are of conceptual importance: the description of a real macrosystem at and near thermal equilibrium becomes more *universal* and *efficient*.

First of all, it becomes possible, following the thermodynamic ideas of Planck and Einstein, to extend the conditions of thermal equilibrium of a macrosystem and thermostat (the zero principle of thermodynamics) for including fluctuations of the intensive parameters of the macrosystem. This generalization involves a tacit assumption, which is not present in the Gibbs approach, that the macrosystem has much fewer degrees of freedom (N_{ob}) than the thermostat (N_{th}), although both objects are certainly macroscopic: N_{ob} , $N_{th} \ge 1$. Concerning the calculations, this implies the existence of the additional small parameter $N_{ob}/N_{th} \ll 1$, which provides for the nonzero fluctuations of the intensive thermodynamic parameters of a macrosystem, while the same parameters of the thermostat remain fixed.

The 'duality' (inherent in the Gibbs approach) is also removed in the treatment of certain physical quantities (for example, the pressure), as either dynamic or thermodynamic parameter depending on what kind of ensemble (isochoric or isobaric) is used for the description of the real macrosystem ⁴¹. It is clear, however, that such a description in principle should not depend on the selection of the Gibbs ensemble, the more so that none of the thermodynamic parameters of the macroscopic system can be fixed with an absolute precision ⁴².

Owing to the uniform thermodynamic treatment of all the stochastic physical quantities characterizing the macrosystem, the Einstein approach manages to do without any analogue of the Gibbs ensemble. Because of this, the description of the macrosystem, and especially the description of the thermodynamic fluctuations, becomes truly *universal*.

As far as the *efficiency* of the description is concerned, Einstein's approach does not require any *a priori* knowledge of the microscopic structure and properties of the macrosystem. The quantities used in this approach (for example, the coefficients of expansion of quasi-equilibrium entropy in fluctuations, of the coefficients linking the fluctuations of extensive and intensive thermodynamic parameters) may be regarded as phenomenological parameters and taken, for example, from experiment. At the same time, in some cases they can be calculated as purely equilibrium quantities in the framework of the Gibbs approach, taking advantage of their proximity to the thermal equilibrium state.

In this way, the macroscopic physical object according to Einstein is 'more stochastic' than that according to Gibbs, which obviously better corresponds to physical reality. In addition, Einstein's description is more universal and efficient, because it does not initially separate the thermodynamic parameters into 'independent' and 'dependent' — instead, they all have equal status, and the selection of 'independent' parameters is just a matter of convenience in computations.

6.2 Prospects of development of statistical thermodynamics

The results obtained are also important in a perspective more general than the solution of the Gibbs and Einstein problems for PFs or the comparison of the two approaches to the description of thermodynamic fluctuations as such. As a matter of fact, these results allow us to make considerable progress in our understanding of the unity of the physical world in the spirit of Planck's momentous ideas. Until recently the main attention in this respect was paid to the description of nature on the microscopic level. In this work we demonstrate the feasibility of a unified approach to the microscopic and macroscopic levels of description, on the one hand, and, on the other hand, the distinctions between each of these levels of description.

On the basis of the above analysis we may formulate the criterion of classification of different versions of the physical picture of the world, common for microscopic and macroscopic levels of description. We believe that such a criterion is the *degree of inclusion of fluctuations* in the theories corresponding to each of the versions of the physical picture of the world ⁴³. We distinguish three such versions: classical, quasi-classical, and properly nonclassical. The first includes the strictly deterministic theories, in which fluctuations are completely absent; the second includes those theories in which only one physical quantity (the extensive variable) in each

⁴¹ In particular, as follows from the results of Section 5.2, the model of the boundary of the system and thermostat in the form of absolutely rigid and fixed 'walls', used in the calculation of PFs in the isochoric Gibbs ensemble, is too much idealized.

⁴² Any such parameter is inevitably subject to fluctuations arising both from the finiteness of the system under consideration and the uncontrollable effects of the thermostat.

⁴³ In an implicit form such a criterion was utilized in the microscopic description in Ref. [40].

pair of canonically or thermodynamically conjugated quantities fluctuates. The third version includes those theories in which fluctuations are exhibited by both the extensive and the conjugate intensive quantities.

In this way, in accordance with this criterion, the consecutive transition from a classical to quasi-classical and then to a nonclassical description is associated with the increasing stochasticity of the physical system and with the greater digression from strict determinism on both the microscopic and macroscopic levels. Schematically, this thesis may be represented by the following table that reflects the conceptual resemblance between different versions of dynamics and thermodynamics.

Version Level	Classical	Quasi-classical	Nonclassical
Microscopic	Classical dynamics (Newton, Maxwell)	Quasi-classical dynamics (Bohr, Sommerfeld)	Nonclassical (quantum) dynamics (Heisenberg, Schrödinger, Dirac)
Macroscopic	Classical thermodynamics (Clausius)	Quasi-classical thermodynamics (Gibbs)	Nonclassical (statistical) thermodynamics (Einstein)

Indeed, the classical version of describing the microscopic and macroscopic objects (the Newton–Maxwell dynamics and the Clausius thermodynamics, respectively) is characterized by a total absence of fluctuations. The Gibbs approach, which accounts for fluctuations of only one (extensive) quantity must then be classified as quasi-classical. In this sense the Gibbs statistical mechanics is similar to the quasiclassical dynamics of Bohr and Sommerfeld⁴⁴.

The results of this work may serve as a basis for making another step and attribute the Einstein statistical thermodynamics to the nonclassical domain, because both conjugate parameters are allowed to fluctuate in this theory. Accordingly, Einstein's statistical thermodynamics is the counterpart of the Heisenberg–Schrödinger–Dirac nonclassical dynamics.

We have to admit, however, that Einstein's approach [3], formulated in 1910, is not yet the final version of statistical thermodynamics, because it relies on certain results from the Gibbs approach and therefore calls for further improvement. Important steps in this direction were made by Szilard [42] in 1925, and later by Mandelbrot [43], Tisza and Quay [44] in the 1950s and 60s (the current state of this problem is discussed in Refs [45–47]). These extensions of Einstein's approach are based on the principles of mathematical statistics and the theory of measurements on macroparameters of a physical object 45 .

The basic idea underlying the direction of development of statistical thermodynamics, proposed in these works, consists in the introduction of a probabilistic description directly on

⁴⁴ Maslov [41] came to the same conclusion from different assumptions.
⁴⁵ Unfortunately, these problems have not won the proper attention of the physical community, compared with the attention enjoyed, for example, by the role of measurements in the description of microscopic objects (see, for example, Refs [48 – 50]).

the *macroscopic* level or in the space of macroparameters, and this does not depend on the availability of any kind of a description of the same object on the *microscopic* level. An example of the efficiency of the totally macroscopic approach is the thermodynamic description of black holes in Ref. [51], which actually contained the prediction of the Hawking quantum effect, whose nature is microscopic.

We believe that such a description gives a more adequate treatment of the *integral properties of a macroscopic object*, which are in principle not possessed by the constituent microobjects (such properties are described, for example, by the intensive thermodynamic parameters). The above analysis of the problem of calculation of pressure and its fluctuations clearly indicates that the results of microscopic and macroscopic descriptions of one and the same physical object coincide far from always.

By this means, in spite of the conceptual correlation between the different versions of the physical picture of the world at the microscopic and macroscopic levels of description, these levels each have their own specific features, and therefore cannot be reduced to one. The ideology of such an approach was expressed (with some polemical pathos) by Mandelbrot [53]: "Our approach ... realizes a dream of the 19th century 'energeticists': to describe matter-in-bulk without reference to atoms. It is a pity that all energeticists have passed a way long ago..."

Generally, this issue ought to be considered in the broader context of the standing debate between the advocates of the 'effective' physical theories, which are conceptually different for every hierarchic level of description of nature, and the champions of the final unified 'theory of everything' ⁴⁶. In this connection it would be interesting to note that, in perfect agreement with our conclusions, the possible discord between the results of statistical mechanics and statistical thermodynamics was pointed out by H A Lorentz in his famous lectures [54] at the College de France in Paris in 1912: "One may conclude that currently the domains of the two methods do not coincide completely, although they have an extensive part in common".

Later on, the inevitability of such discord was pointed out by V A Fock and N S Krylov [55]: "One may assume that between the macroscopic characteristic and the conventional microscopic description there is some kind of complementarity, similar to that which, according to quantum mechanics, arises in the case of the classical description. A too precise definition of the system position within the phase region selected by the macroscopic state is not possible without violating the macroscopic characteristic of the system."

A similar sentiment was expressed by R B Laughlin in his Nobel lecture (1998) [1]: "I myself have came to suspect that all the important outstanding problems in physics are emergent in nature, including quantum gravity". It is quite possible, as it has been more than once in the history of physics, that currently the development of science is undergoing the next 'spiral' on the way towards the construction of a comprehensive physical picture of the world. There is good reason to believe that the priority on this way will belong to the 'effective' physical theories.

We wish to pay homage to the memory of Boris Valentinovich Medvedev, who played a great role in our life

⁴⁶ Recent arguments in favor of each of these standpoints are discussed, for example, in Ref. [52].

and scientific work. Discussions with B V Medvedev about the role of fluctuations in drawing the boundary between classical and nonclassical physics much stimulated this research.

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7. Appendix. Proof of the generalized Bogolyubov – Zubarev theorem

1. Let us calculate the left-hand side of equality (3.8) at n = 1. Differentiating (3.3) with respect to the volume *V*, and using the properties (3.6) and (3.7), we get

$$\frac{\partial \mathcal{Z}_{V}^{(\varepsilon)}}{\partial V} = \int d\Gamma \frac{\partial}{\partial V} \Big\{ \exp\left[-\beta \mathcal{H}_{V}^{(\varepsilon)}(\Gamma)\right] \Big\}$$
$$= -\beta \int d\Gamma \frac{\partial \mathcal{H}_{V}^{(\varepsilon)}(\Gamma)}{\partial V} \exp\left[-\beta \mathcal{H}_{V}^{(\varepsilon)}(\Gamma)\right]$$
$$= -\beta \int_{\dots V \dots} \frac{\partial \mathcal{H}_{V}^{(\varepsilon)}(\Gamma)}{\partial V} \exp\left[-\beta \mathcal{H}^{(0)}(\Gamma)\right].$$
(7.1)

Going to the limit $\varepsilon \to +0$ and accounting for definition (2.15), we find the left-hand side of Eqn (3.8):

$$\lim_{\varepsilon \to +0} \frac{\partial \mathcal{Z}_{V}^{(\varepsilon)}}{\partial V} = \beta \int_{\dots V_{\dots}} d\Gamma \,\tilde{P}^{(0)}(\Gamma) \,\exp\left[-\beta \mathcal{H}^{(0)}(\Gamma)\right].$$
(7.2)

2. To calculate the right-hand side of equality (3.8), we take into account the variation of the volume V within the limits of integration in Eqn (3.4), by introducing the coefficient λ^f (where $\lambda \neq 0$ is a real number):

$$\mathcal{Z}^{(0)}(\lambda^{f}V) = \int_{\dots\lambda^{f}V\dots} d\Gamma \exp\left[-\beta \mathcal{H}^{(0)}(\Gamma)\right].$$
(7.3)

Then

$$\frac{\partial \mathcal{Z}^{(0)}(\lambda^{f}V)}{\partial \lambda} = \frac{\partial \mathcal{Z}^{(0)}(\lambda^{f}V)}{\partial (\lambda^{f}V)} \frac{\partial (\lambda^{f}V)}{\partial \lambda} = \frac{V}{\lambda} \frac{\partial \mathcal{Z}^{(0)}(\lambda^{f}V)}{\partial V} .$$
(7.4)

Setting in this equality $\lambda = 1$, we get

$$\frac{\partial \mathcal{Z}^{(0)}(V)}{\partial V} = \frac{1}{fV} \left. \frac{\partial \mathcal{Z}^{(0)}(\lambda^f V)}{\partial \lambda} \right|_{\lambda=1}.$$
(7.5)

For calculating the derivative in the right-hand side of Eqn (7.3), it is convenient to eliminate the dependence on λ in the limits of integration in (7.3), and move it into the integrand. As shown in Refs [9, 10], this is accomplished by applying the consistent canonical scale transformation (3.9a) to variables p and q in Γ , so that $(\lambda^f V') = \lambda^f (V/\lambda^f) = V$, and

$$d\Gamma' = \frac{dp' \, dq'}{N! (2\pi\hbar)^{fN}} = \frac{dp \, dq}{N! (2\pi\hbar)^{fN}} = d\Gamma.$$
(7.6)

Substituting the transformed Hamiltonian function (3.9b) into the right-hand side of Eqn (7.3), taking (7.6) into account, and replacing the variables $p' \rightarrow p$, $q' \rightarrow q$ in the

integrand, we finally get

$$\mathcal{Z}^{(0)}(\lambda^{f}V) = \int_{\dots V\dots} d\Gamma \exp\left[-\beta \mathcal{H}^{(0)}(p/\lambda,\lambda q)\right].$$
(7.7)

Differentiating (7.7) with respect to λ , we find

$$\frac{\partial \mathcal{Z}^{(0)}(\lambda^{f}V)}{\partial \lambda} = \int_{\dots V_{\dots}} d\Gamma \frac{\partial}{\partial \lambda} \exp\left[-\beta \mathcal{H}^{(0)}(p/\lambda, \lambda q)\right]$$
$$= \beta \int_{\dots V_{\dots}} d\Gamma \left(-\frac{\partial \mathcal{H}^{(0)}(p/\lambda, \lambda q)}{\partial \lambda}\right)$$
$$\times \exp\left[-\beta \mathcal{H}^{(0)}(p/\lambda, \lambda q)\right].$$
(7.8)

Setting $\lambda = 1$ in both parts of this equality, and using relation (7.5), we find the expression for the right-hand side of equality (3.8) at n = 1:

$$\frac{\partial \mathcal{Z}^{(0)}(V)}{\partial V} = \frac{\beta}{fV} \int_{\dots V_{\dots}} d\Gamma \left(-\frac{\partial \mathcal{H}^{(0)}(p/\lambda, \lambda q)}{\partial \lambda} \Big|_{\lambda=1} \right) \\ \times \exp\left[-\beta \mathcal{H}^{(0)}(p, q) \right].$$
(7.9)

Equating, according to (3.8), expressions (7.2) and (7.9), we come to the sought expression (3.1) for the classical DEOS-I, which completes the proof of the Bogolyubov–Zubarev theorem as such.

3. Proceeding by analogy with paragraphs 1 and 2, we shall calculate the left-hand side of equality (3.8) at n = 2. Differentiating (7.1) with respect to the volume *V*, and using the properties (3.6) and (3.7), we get

$$\frac{\partial^{2} \mathcal{Z}_{V}^{(\varepsilon)}}{\partial V^{2}} = -\beta \int_{\dots V...} d\Gamma \left\{ \frac{\partial^{2} \mathcal{H}_{V}^{(\varepsilon)}(\Gamma)}{\partial V^{2}} - \beta \left(\frac{\partial \mathcal{H}_{V}^{(\varepsilon)}(\Gamma)}{\partial V} \right)^{2} \right\} \\ \times \exp \left[-\beta \mathcal{H}_{V}^{(0)}(\Gamma) \right].$$

Going to the limit $\varepsilon \to +0$ in this expression, and using definitions (2.15) and (2.16), we get in the upshot:

$$\lim_{e \to +0} \frac{\partial^2 \mathcal{Z}_V^{(e)}}{\partial V^2} = -\beta \int_{\dots V_{\dots}} d\Gamma \Big\{ \tilde{\Psi}_V^{(0)}(\Gamma) - \beta \big(\tilde{P}_V^{(0)}(\Gamma) \big)^2 \Big\} \\ \times \exp \big[-\beta \mathcal{H}_V^{(0)}(\Gamma) \big]$$
(7.10)

4. Let us calculate the right-hand side of equality (3.8) at n = 2. Differentiating with respect to λ the equations of linkage (7.4) between the first derivatives of $\mathcal{Z}^{(0)}(\lambda^f V)$ with respect to λ and V, and assuming that the second (mixed) derivatives with respect to these variables are equal, we find

$$\frac{\partial^2 \mathcal{Z}^{(0)}(\lambda^f V)}{\partial \lambda^2} = (f-1) \frac{fV}{\lambda^2} \frac{\partial \mathcal{Z}^{(0)}(\lambda^f V)}{\partial V} + \left(\frac{fV}{\lambda}\right)^2 \frac{\partial^2 \mathcal{Z}^{(0)}(\lambda^f V)}{\partial V^2}.$$

Setting $\lambda = 1$, we get

$$\frac{\partial^2 \mathcal{Z}^{(0)}(V)}{\partial V^2} = \frac{1}{\left(fV\right)^2} \left. \frac{\partial^2 \mathcal{Z}^{(0)}(\lambda^f V)}{\partial \lambda^2} \right|_{\lambda=1} - \frac{f-1}{fV} \left. \frac{\partial \mathcal{Z}^{(0)}(V)}{\partial V} \right|_{\lambda=1}.$$
(7.11)

Differentiating repeatedly the derivative (7.8) with respect to λ , and then setting $\lambda = 1$, we arrive at

$$\begin{split} \frac{\partial^{2} \mathcal{Z}^{(0)}(\lambda^{f} V)}{\partial \lambda^{2}} \bigg|_{\lambda=1} &= -\beta \int_{\dots V \dots} d\Gamma \bigg\{ -\frac{\partial^{2} \mathcal{H}^{(0)}(p/\lambda, \lambda q)}{\partial \lambda^{2}} \bigg|_{\lambda=1} \\ &- \beta \bigg(-\frac{\partial \mathcal{H}^{(0)}(p/\lambda, \lambda q)}{\partial \lambda} \bigg)^{2} \bigg|_{\lambda=1} \bigg\} \\ &\times \exp \big[-\beta \mathcal{H}^{(0)}(\Gamma) \big] \,. \end{split}$$

Substituting this expression into Eqn (7.11) and using Eqn (7.5) together with definition (3.1), for the right-hand side of equality (3.8) at n = 2 we get

$$\frac{\partial^{2} \mathcal{Z}^{(0)}(V)}{\partial V^{2}} = -\beta \int_{\dots V...} d\Gamma \exp\left[-\beta \mathcal{H}^{(0)}(\Gamma)\right] \\ \times \left\{ \frac{1}{(fV)^{2}} \frac{\partial^{2} \mathcal{H}^{(0)}(p/\lambda, \lambda q)}{\partial \lambda^{2}} \Big|_{\lambda=1} - \beta \left(\widetilde{P}_{V}^{(0)}(\Gamma)\right)^{2} \\ + \frac{1}{V} \widetilde{P}_{V}^{(0)}(\Gamma) + \frac{1}{(fV)^{2}} \frac{\partial \mathcal{H}^{(0)}(p/\lambda, \lambda q)}{\partial \lambda} \Big|_{\lambda=1} \right\}.$$
(7.12)

Equating, according to (3.8), expressions (7.10) and (7.12), we find the sought expression (3.2) for the classical DEOS-II, which is an extension of the Bogolyubov–Zubarev theorem.

5. Let us derive expressions (3.12) and (3.13) for the additive Hamiltonian function

$$\mathcal{H}(p,q) = \mathcal{H}(p) + \mathcal{H}(q) \tag{7.13}$$

with the homogeneous functions of the form (3.11); to simplify the notation we drop out the superscript (0) everywhere.

For the first derivatives we have

$$\frac{\partial \mathcal{H}(p/\lambda)}{\partial \lambda} = -\frac{k}{\lambda} \mathcal{H}(p/\lambda), \quad \frac{\partial \mathcal{H}(\lambda q)}{\partial \lambda} = \frac{l}{\lambda} \mathcal{H}(\lambda q), \quad (7.14)$$

so that

$$\frac{\partial \mathcal{H}(p/\lambda)}{\partial \lambda}\Big|_{\lambda=1} + \frac{\partial \mathcal{H}(\lambda q)}{\partial \lambda}\Big|_{\lambda=1} = -k\mathcal{H}(p) + l\mathcal{H}(q), \quad (7.15)$$

whence follows (3.12) with due account for Eqn (3.1).

For the second derivatives, differentiating (7.14), we find

$$\frac{\partial^2 \mathcal{H}(p/\lambda)}{\partial \lambda^2} = \frac{1}{\lambda^2} \, k(1+k) \, \mathcal{H}(p/\lambda) \,,$$
$$\frac{\partial^2 \mathcal{H}(\lambda q)}{\partial \lambda^2} = \frac{1}{\lambda^2} \, l(l-1) \, \mathcal{H}(\lambda q) \,,$$

so that

$$\frac{\partial^{2} \mathcal{H}(p/\lambda)}{\partial \lambda^{2}} \bigg|_{\lambda=1} + \frac{\partial^{2} \mathcal{H}(\lambda q)}{\partial \lambda^{2}} \bigg|_{\lambda=1}$$
$$= k(1+k) \mathcal{H}(p) + l(l-1) \mathcal{H}(q). \quad (7.16)$$

Evidently, expressions (7.15) and (7.16) contain terms of the same order that cancel out exactly, and we finally get

$$\frac{\partial^{2} \mathcal{H}(p/\lambda,\lambda q)}{\partial \lambda^{2}}\Big|_{\lambda=1} + \frac{\partial \mathcal{H}(p/\lambda,\lambda q)}{\partial \lambda}\Big|_{\lambda=1} = k^{2} \mathcal{H}(p) + l^{2} \mathcal{H}(q),$$

whence follows (3.13) with due account for definition (3.2).

References

- Laughlin R B *Rev. Mod. Phys.* **71** 863 (1999) [*Usp. Fiz. Nauk* **170** 292 (2000)]; Störmer H L *Rev. Mod. Phys.* **71** 875 (1999) [*Usp. Fiz. Nauk* **170** 304 (2000)]
- Gibbs J W Elementary Principles in Statistical Mechanics (New York: C. Scribner's Sons, 1902) [Translated into Russian (Moscow: Nauka, 1982)]
- Einstein A Ann. Phys.-Leipzig 33 1275 (1910) [Translated into Russian in Izbrannye Sochineniya Vol. 3 (Moscow: Nauka, 1966) p. 216]
- 4. Kittel C *Phys. Today* **41** (5) 93 (1988)
- 5. Mandelbrot B Phys. Today 42 (1) 71 (1989)
- Planck M Einführung in die Theoretisch Physik Vol. 5 Einführung in die Theorie der Wärme (Leipzig: Verlag von S. Hirzel, 1930) [Translated into Russian (Moscow-Leningrad: ONTI, 1935) Ch. 5] [Translated into English as Introduction to Theoretical Physics Vol. 5 Theory of Heat (New York: Macmillan, 1949)]
- Landau L D, Lifshitz E M Statisticheskaya Fizika Part I (Statistical Physics) 3rd ed. (Moscow: Nauka, 1976) [Translated into English (Oxford: Pergamon Press, 1980)]
- Münster A Physica 26 1117 (1960); Nuovo Cimento Suppl. 13 (1960); Statistical Thermodynamics Vol. 1, 2nd ed. (Berlin: Springer-Verlag, 1969)
- Bogolyubov N N "Kvazisrednie v zadachakh statisticheskoĭ mekhaniki" ("Quasi-means in problems of statistical mechanics"), Preprint OIYaID-781 (Dubna: OIYaI, 1961); *Izbrannye Trudy* (Selected Works) Vol. 3 (Kiev: Naukova Dumka, 1971) [Translated into English (New York: Gordon and Breach, 1990–1991)]
- Bogolyubov N N Problemy Dinamicheskoĭ Teorii v Statisticheskoĭ Fizike (Dynamical Theory Problems in Statistical Physics) (Moscow-Leningrad: Gostekhizdat, 1946); Izbrannye Trudy (Selected Works) Vol. 2 (Kiev: Naukova Dumka, 1970) [Translated into English (New York: Gordon and Breach, 1990–1991)]
- Zubarev D N Neravnovesnaya Statisticheskaya Termodinamika (Nonequilibrium Statistical Thermodynamics) (Moscow: Nauka, 1971) [Translated into English (New York: Consultants Bureau, 1974)]
- Hellmann H G A Kvantovaya Khimiya (Quantum Chemistry) (Moscow-Leningrad: GITTL, 1937); a revised and compact edition in German Einführung in die Quantenchemie (Leipzig, Wien: F. Deuticke, 1937)
- Feynman R P Phys. Rev. 56 340 (1939); Feynman R P Statistical Mechanics (Reading, Mass.: W. A. Benjamin, 1972) [Translated into Russian (Moscow: Mir, 1975)]
- 14. Leontovich M A *Statisticheskaya Fizika* (Statistical Physics) 2nd ed. (Moscow: Nauka, 1983)
- Levich V G Kurs Teoreticheskoĭ Fiziki (Course in Theoretical Physics) Vol. 1, 2nd ed. (Moscow: Nauka, 1969) [Translated into English: Theoretical Physics Vol. 1, 2 (Amsterdam: North-Holland, 1970)]
- Kubo R Statistical Mechanics (Amsterdam: North-Holland, 1965) [Translated into Russian (Moscow: Mir, 1967)]
- Ansel'm A I Osnovy Statisticheskoĭ Fiziki i Termodinamiki (Foundations of Statistical Physics and Thermodynamics) (Moscow: Nauka, 1973)
- Heer C V Statistical Mechanics, Kinetic Theory, and Stochastic Processes (New York: Academic Press, 1972) [Translated into Russian (Moscow: Mir, 1976)]
- Rumer Yu B, Ryvkin M Sh *Termodinamika, Statisticheskaya Fizika i Kinetika* (Thermodynamics, Statistical Physics and Kinetics) 2nd ed. (Moscow: Nauka, 1977) [Translated into English (Moscow: Mir, 1980)]
- 20. Kuni F M *Statisticheskaya Fizika i Termodinamika* (Statistical Physics and Thermodynamics) (Moscow: Nauka, 1981)
- Kvasnikov I A Termodinamika i Statisticheskaya Fizika. Teoriya Ravnovesnykh Sistem (Thermodynamics and Statistical Physics. Theory of Equilibrium Systems) (Moscow: Izd. MGU, 1991); Teoriya Neravnovesnykh Sistem (Theory of Nonequilibrium Systems) (Moscow: Izd. MGU, 1987)
- 22. Kondrat'ev A S, Romanov V P Zadachi po Statisticheskoĭ Fizike (Problems in Statistical Physics) (Moscow: Nauka, 1992)

- Sommerfeld A Vorlesungen über Theoretische Physik Bd. 5 Thermodynamik und Statistik (Diederich: Wiesbaden, 1952) [Translated into Russian (Moscow: IL, 1955)] [Translated into English as Lectures on Theoretical Physics Vol. 5 Thermodynamics and Statistical Mechanics (New York: Academic Press, 1956)]
- Mayer J E, Goeppert-Mayer M Statistical Mechanics 2nd ed. (New York: Wiley, 1977) [Translated into Russian: (Moscow: Mir, 1980)]
- Hill T L Statistical Mechanics (New York: McGraw-Hill Book Co., 1956) [Translated into Russian (Moscow: IL, 1960)]
- Huang K Statistical Mechanics (New York: John Wiley & Sons, 1963) [Translated into Russian (Moscow: Mir, 1966)]
- Isihara A Statistical Physics (New York: Academic Press, 1971) [Translated into Russian (Moscow: Mir, 1973)]
- Kittel Ch *Thermal Physics* (New York: John Wiley and Sons, 1969) [Translated into Russian (Moscow: Nauka, 1977)]
- Reif F Statistical Physics (Berkeley Physics Course, Vol. 5) (New York: McGraw-Hill Book Co., 1965) 2nd ed. [Translated into Russian: (Moscow: Nauka, 1977)]
- Klimontovich Yu L Statisticheskaya Fizika (Statistical Physics) (Moscow: Nauka, 1982) [Translated into English (Chur, Switzerland: Harwood Acad. Publ., 1986)]
- Terletskii Ya P Statisticheskaya Fizika (Statistical Physics) 3rd ed. (Moscow: Vysshaya Shkola, 1994) [Translated into English (Amsterdam: North-Holland, 1971)]
- 32. Fowler R H *Statistical Mechanics* 2nd ed. (Cambridge: Cambridge Univ. Press, 1936)
- 33. Wergeland H Det. Kgl. Norske Vidensk. Forh. 28 (21) 106 (1955)
- 34. Klein M J Physica 26 1073 (1960)
- Lindhard J, in *The Lesson of Quantum Theory* (Eds J de Boer, E Dal, O Ulfbeck) (Amsterdam: North-Holland, 1986)
- 36. Greene R F, Callen H B Phys. Rev. 83 1231 (1951)
- 37. Jaynes E T Phys. Rev. 106 620 (1957); 108 171 (1957)
- Venttsel' E S *Teoriya Veroyatnostei* (Probability Theory) 5th ed. (Moscow: Vysshaya Shkola, 1998)
- Vladimirov V S Obobshchennye Funktsii v Matematicheskoĭ Fizike (Generalized Functions in Mathematical Physics) (Moscow: Nauka, 1976)
- Faddeev L D, Yakubovskii O A Lektsii po Kvantovoi Mekhanike dlya Studentov-Matematikov (Lectures on Quantum Mechanics for Students in Mathematics) (Leningrad: Izd. LGU, 1980)
- 41. Maslov V P Funktsional'nyĭ Analiz 28 28 (1994); Teor. Mat. Fiz. 101 433 (1994) [Theor. Math. Phys. 101 1466 (1994)]
- 42. Szilard L Z. Phys. 32 753 (1925)
- 43. Mandelbrot B C. R. Acad. Sci. 243 1835 (1956); J. Math. Phys. 5 164 (1964)
- 44. Tisza L, Quay P M Ann. Phys. New York 25 48 (1963)
- Schlögl F Ann. Phys. Leipzig 45 155 (1963); Phys. Rep. 62 267 (1980); J. Phys. Chem. Solids 49 679 (1988)
- Lavenda B H Int. J. Theor. Phys. 26 1069 (1987); 27 451 (1988); Lavenda B H Statistical Physics: Probabilistic Approach (New York: Wiley, 1991) [Translated into Russian (Moscow: Mir, 1999)]
- 47. Uffink J, van Lith J *Found*. *Phys.* **28** 323 (1998)
- Kadomtsev B B *Dinamika i Informatsiya* (Dynamics and Information) (Moscow: Red. Zh. "Usp. Fiz. Nauk", 1997)
- Klyshko D N Usp. Fiz. Nauk 168 975 (1998) [Phys. Usp. 41 885 (1998)]
- Mensky M B Usp. Fiz. Nauk 168 1017 (1998) [Phys. Usp. 41 923 (1998)]; Menskii M B 170 631 (2000) [Phys. Usp. 43 585 (2000)]
- 51. Beckenstein J Phys. Rev. D 7 2333 (1973); 9 3292 (1974)
- Isaev P S, Mamchur E A Usp. Fiz. Nauk 170 1025 (2000) [Phys. Usp. 43 953 (2000)] [Review of the book: Conceptual Foundations of Quantum Field Theory (Ed. Tian Yu Cao) (Cambridge: Cambridge Univ. Press, 1999)]
- 53. Mandelbrot B Ann. Math. Stat. 33 1021 (1962)
- Lorentz H A Les Theories Statistiques en Thermodinamique (Leipzig-Berlin: B.G. Teubner, 1916) [Translated into Russian (Leningrad-Moscow: ONTI, 1935)]
- 55. Fock V A "Preface", in Krylov N S Raboty po Obosnovaniyu Statisticheskoĭ Fiziki (Works on Validation of Statistical Physics) (Moscow-Leningrad: Izd. AN SSSR, 1950); see also Krylov N S Works on the Foundations of Statistical Physics (Princeton, N.J.: Princeton Univ. Press, 1979)