

THERMODYNAMICS OF FEW-PARTICLE SYSTEMS

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We consider the wide class of few-particle systems that have some analog of the thermodynamic laws. These systems are characterized by the distributions that are determined by the Hamiltonian and satisfy the Liouville equation. Few-particle systems of this class are described by a non-holonomic constraint: the power of non-potential forces is directly proportional to the velocity of the elementary phase volume change. The coefficient of this proportionality is determined by the Hamiltonian. In the general case, the examples of the few-particle systems of this class are the constant temperature systems, canonical-dissipative systems, and Fermi–Bose classical systems.

Keywords: Thermodynamic laws; few-particle system; non-holonomic constraint.

1. Introduction

The main aim of statistical thermodynamics is to derive the thermodynamic properties of systems starting from a description of the motion of the particles. Statistical thermodynamics of few-particle systems have recently been employed to study a wide variety of problems in the field of molecular dynamics. In molecular dynamics calculations, few-particle systems can be exploited to generate statistical ensembles as the canonical, isothermal-isobaric and isokinetic ensembles.^{1–8} The aim of this work is the extension of the statistical thermodynamics to a wide class of few-particle systems. We can point out some few-particle systems that have some analog of thermodynamics laws.

- The constant temperature systems with minimal Gaussian constraint are considered in Refs. 1–4 and 7. These systems are the few-particle systems that are defined by the non-potential forces in the form $\mathbf{F}_i^{(n)} = -\gamma\mathbf{p}_i$ and the Gaussian non-holonomic constraint. This constraint can be represented as an addition term to the non-potential force.
- The canonical distribution can be derived as a stationary solution of the Liouville equation for a wide class of few-particle system.¹² This class is defined by a very simple condition for the non-potential forces: the power of the non-potential forces must be directly proportional to the velocity of the Gibbs phase

(elementary phase volume) change. This condition defines the general constant temperature systems. This condition leads to the canonical distribution as a stationary solution of the Liouville equations. For the linear friction, we derived the constant temperature systems. The general form of the non-potential forces is not considered in Ref. 12.

- The canonical-dissipative systems are described in Refs. 9 and 10. These systems are the few-particle systems that are defined by the non-potential forces $\mathbf{F}_i^{(n)} = -\partial G(H)/\partial \mathbf{p}_i$ where $G(H)$ is a function of Hamiltonian H . The distribution functions are derived as solutions the Fokker–Planck equation. Note that Fokker–Planck equation can be derived from the Liouville equation.¹¹
- The quantum few-particle systems with pure stationary states are suggested in Refs. 13 and 14. The correspondent classical systems are not discussed.
- The few-particle systems with the fractional phase space and non-Gaussian distributions are suggested in Refs. 15 and 16. Note that nondissipative systems with the usual phase space are dissipative systems in the fractional phase space.^{15,16}

The analog of the first law of thermodynamics is connected with the variation of the mean value Hamiltonian

$$U(x) = \int H(\mathbf{q}, \mathbf{p}, x) \rho(\mathbf{q}, \mathbf{p}, x) d^N \mathbf{q} d^N \mathbf{p} \quad (1)$$

that has the form

$$dU(x) = \int \delta_x H \rho d^N \mathbf{q} d^N \mathbf{p} + \int H \delta_x \rho d^N \mathbf{q} d^N \mathbf{p}.$$

We can have the analog of the second laws of thermodynamics if the second term on the right-hand side can be represented in the form

$$T(x) dS(x) = T(x) \delta_x \int S_N(\rho) \rho d^N \mathbf{q} d^N \mathbf{p}.$$

In this case, we have the condition

$$H \delta_x \rho = T(x) \delta_x (\rho S_N(\rho)).$$

This representation is realized if the distribution ρ can be represented as a function of Hamiltonian $\rho = \rho(H, x)$ such that we can write $H = T(x)G(\rho)$. Obviously, we have the second requirement for this distribution: the distribution ρ satisfy the Liouville equation of the systems. For these N -particle systems, we can use the analogs of the usual thermodynamics laws. Note that N is an arbitrary natural number since we do not use the condition $N \gg 1$ or $N \rightarrow \infty$. This allows us to use the suggested few-particle systems for the simulation schemes¹⁷ for the molecular dynamics.

In this paper we consider few-particle systems with distributions that are defined by Hamiltonian and Liouville equation. We describe the few-particle systems that have some analog of the thermodynamic laws. These systems can be defined by the non-holonomic (non-integrable) constraint: the power of non-potential forces

is directly proportional to the velocity of the elementary phase volume change. In the general case, the coefficient of this proportionality is determined by the Hamiltonian. The special constraint allows us to derive distributions for the system, even in far-from equilibrium states. The examples of these few-particle systems are the constant temperature systems,^{1–8} the canonical-dissipative systems,^{9,10} and the Fermi–Bose classical systems.⁹

In Sec. 2, we derive the analog of thermodynamic laws for the few-particle systems with the distributions that are defined by Hamiltonian. In Sec. 3, we consider the condition for the non-potential forces that allows us to use the analog of thermodynamic laws. We consider the wide class of few-particle systems with canonical Gibbs distribution and non-Gaussian distributions. In Sec. 4, we consider the non-holonomic constraint for few-particle systems. We formulate the proposition which allows us to derive the thermodynamic few-particle systems from the equations of few-particle system motion. The few-particle systems with the simple Hamiltonian and the simple non-potential forces are considered. Finally, a short conclusion is given in Sec. 5.

2. Thermodynamics Laws

2.1. First thermodynamics law

Let us consider the N -particle classical system in the Hamilton picture and denote the position of the i th particle by \mathbf{q}_i and its momentum by \mathbf{p}_i , where $i = 1, \dots, N$. The state of this system is described by the distribution function $\rho = \rho(\mathbf{q}, \mathbf{p}, x, t)$.

The mean value of the function $f(\mathbf{q}, \mathbf{p}, x, t)$ is defined by the following equation

$$f(x, t) = \int f(\mathbf{q}, \mathbf{p}, x, t) \rho(\mathbf{q}, \mathbf{p}, x, t) d^N \mathbf{q} d^N \mathbf{p}. \tag{2}$$

Here, $x = \{x_1, x_2, \dots, x_n\}$ are external parameters. The variation δ_x for this function can be defined by the relation

$$\delta_x f(\mathbf{q}, \mathbf{p}, x, t) = \sum_{k=1}^n \frac{\partial f(\mathbf{q}, \mathbf{p}, x, t)}{\partial x_k} dx_k. \tag{3}$$

The first law of thermodynamics states that the internal energy $U(x)$ may change because of (1) heat transfer δQ , and (2) work δA of thermodynamics forces $X_k(x)$:

$$\delta A = \sum_{k=1}^n X_k(x) dx_k. \tag{4}$$

The external parameters x here act as generalized coordinates. In the usual equilibrium thermodynamics the work done does not entirely account for the change in the internal energy $U(x)$. The internal energy also changes because of the transfer of heat, and so

$$dU = \delta Q - \delta A. \tag{5}$$

Since thermodynamic forces $X_k(x)$ are non-potential forces

$$\frac{\partial X_k(x)}{\partial x_l} = \frac{\partial X_l(x)}{\partial x_k}, \tag{6}$$

the amount of work δA depends on the path of transition from one state in parameters space to another. For this reason δA and δQ , taken separately, are not total differentials.

Let us give statistical definitions of internal energy, thermodynamic forces and heat transfer for the few-particle systems in the mathematical expression of the analog of the first thermodynamics law. It would be natural to define the internal energy as the mean value of Hamiltonian H :

$$U(x) = \int H(\mathbf{q}, \mathbf{p}, x) \rho(\mathbf{q}, \mathbf{p}, x) d^N \mathbf{q} d^N \mathbf{p}. \tag{7}$$

It follows that the expression for the total differential has the form

$$dU(x) = \int \delta_x H(\mathbf{q}, \mathbf{p}, x) \rho(\mathbf{q}, \mathbf{p}, x) d^N \mathbf{q} d^N \mathbf{p} + \int H(\mathbf{q}, \mathbf{p}, x) \delta_x \rho(\mathbf{q}, \mathbf{p}, x) d^N \mathbf{q} d^N \mathbf{p}.$$

Using Eq. (3), we have

$$dU(x) = \int \frac{\partial H(\mathbf{q}, \mathbf{p}, x)}{\partial x_k} \delta x_k \rho(\mathbf{q}, \mathbf{p}, x) d^N \mathbf{q} d^N \mathbf{p} + \int H(\mathbf{q}, \mathbf{p}, x) \delta_x \rho(\mathbf{q}, \mathbf{p}, x) d^N \mathbf{q} d^N \mathbf{p}. \tag{8}$$

In the first term on the right-hand side we can use the definition of phase density of the thermodynamic force

$$X_k^d(\mathbf{q}, \mathbf{p}, x) = - \frac{\partial H(\mathbf{q}, \mathbf{p}, x)}{\partial x_k}.$$

The thermodynamic force $X_k(x)$ is the mean value of the phase density of the thermodynamics force

$$X_k(x) = \int X_k^d(\mathbf{q}, \mathbf{p}, x) \rho(\mathbf{q}, \mathbf{p}, x) d^N \mathbf{q} d^N \mathbf{p}. \tag{9}$$

Using this equation we can prove the relation (6).

Analyzing these expressions we see that the first term on the right-hand side of the differential (8) answers for the work of thermodynamics forces (9), whereas the amount of the heat transfer is given by

$$\delta Q = \int H(\mathbf{q}, \mathbf{p}, x) \delta_x \rho(\mathbf{q}, \mathbf{p}, x) d^N \mathbf{q} d^N \mathbf{p}. \tag{10}$$

We see that the heat transfer term accounts for the change in the internal energy due not to the work of thermodynamics forces, but rather to the change in the distribution function caused by the external parameters x .

2.2. Second thermodynamics law

Now let us turn our attention to the analog of the second law for the few-particle systems.

The second law of thermodynamics has the form

$$\delta Q = T(x)dS(x). \quad (11)$$

This implies that there exists a function of state $S(x)$ called entropy. The function $T(x)$ acts as an integration factor. Let us prove that the law (11) follows from the statistical definition of δQ in Eq. (10). For Eq. (10), we take the distribution that is defined by the Hamiltonian, and show that Eq. (10) can be reduced to Eq. (11).

We can have the analog of the second laws of thermodynamics if the right-hand side of Eq. (10) can be represented in the form

$$T(x)dS(x) = T(x)\delta_x \int \rho(\mathbf{q}, \mathbf{p}, x) S_N(\rho(\mathbf{q}, \mathbf{p}, x)) d^N \mathbf{q} d^N \mathbf{p}.$$

This requirement can be written in an equivalent form

$$H\delta_x \rho = T(x)\delta_x(\rho S_N(\rho)).$$

This representation is realized if the distribution ρ can be represented as a function of Hamiltonian

$$\rho(\mathbf{q}, \mathbf{p}, x) = \rho(H(\mathbf{q}, \mathbf{p}, x), x). \quad (12)$$

Obviously, we have the second requirement for the distribution ρ which must satisfies the Liouville equation. We assume that Eq. (12) can be solved in the form

$$H = T(x)G(\rho),$$

where G depends on the distribution ρ . The function $T(x)$ is a function of the parameters $x = \{x_1, x_2, \dots, x_n\}$. As the result, we can rewrite Eq. (10) in the equivalent form

$$\delta Q = \int (T(x)G(\rho(\mathbf{q}, \mathbf{p}, x), x) + H_0(x))\delta_x \rho(\mathbf{q}, \mathbf{p}, x) d^N \mathbf{q} d^N \mathbf{p}. \quad (13)$$

The term with $H_0(x)$, which is added into this equation, is equal to zero because of the normalization condition of distribution function ρ :

$$H_0(x)\delta_x \int \rho(\mathbf{q}, \mathbf{p}, x) d^N \mathbf{q} d^N \mathbf{p} = H_0(x)\delta_x 1 = 0.$$

For canonical Gibbs distribution

$$\rho = \frac{1}{Z(x)} \exp -\frac{H(\mathbf{q}, \mathbf{p}, x)}{kT(x)},$$

where $Z(x)$ is defined by

$$Z(x) = \int \exp -\frac{H(\mathbf{q}, \mathbf{p}, x)}{kT(x)} d^N \mathbf{q} d^N \mathbf{p},$$

we use $G(\rho)$ and $H_0(x)$ in the form

$$H_0(x) = kT(x) \ln Z(x) - kT(x), \quad G(\rho) = -k \ln(Z(x)\rho).$$

As a result, Eq. (13) can be rewritten in the form

$$\delta Q = T(x)\delta_x \int \rho(\mathbf{q}, \mathbf{p}, x) S_N(\rho(\mathbf{q}, \mathbf{p}, x)) d^N \mathbf{q} d^N \mathbf{p}, \tag{14}$$

where the function $S_N(\rho)$ is defined by

$$\frac{\partial(\rho S_N(\rho))}{\partial \rho} = G(\rho) + H_0(x)/T(x). \tag{15}$$

We see that the expression for δQ is integrable. If we take $1/T(x)$ for the integration factor, thus identifying $T(x)$ with the analog of absolute temperature, then, using Eqs. (11) and (14), we can give the statistical definition of entropy:

$$S(x) = \int \rho(\mathbf{q}, \mathbf{p}, x) S_N(\rho(\mathbf{q}, \mathbf{p}, x)) d^N \mathbf{q} d^N \mathbf{p} + S_0. \tag{16}$$

Here S_0 is the contribution to the entropy which does not depend on the variables x , but may depend on the number of particles N in the system. As a result the expression for entropy is equivalent to the mean value of phase density function $S^d(\mathbf{q}, \mathbf{p}, x) = S(\rho(\mathbf{q}, \mathbf{p}, x)) + S_0$. Here S^d is a function of dynamic variables \mathbf{q}, \mathbf{p} , and the parameters $x = \{x_1, x_2, \dots, x_n\}$. The number N is an arbitrary natural number since we do not use the condition $N \gg 1$ or $N \rightarrow \infty$. Note that in the usual equilibrium thermodynamics the function $T(x)$ is a mean value of kinetic energy. In the suggested thermodynamics of few-particle systems $T(x)$ is the usual function of the external parameters $x = \{x_1, x_2, \dots, x_n\}$.

2.3. Thermodynamic few-particle systems

Let us define the special class of the few-particle systems with distribution functions that are completely characterized by the Hamiltonian. These distributions must satisfy the Liouville equation for the few-particle system.

Definition A few-particle system

$$\frac{d\mathbf{q}_i}{dt} = \frac{\partial H}{\partial \mathbf{p}_i}, \quad \frac{d\mathbf{p}_i}{dt} = -\frac{\partial H}{\partial \mathbf{q}_i} + \mathbf{F}_i^{(n)}$$

will be called a thermodynamic few-particle system if the following conditions are satisfied:

- (1) the distribution function ρ is determined by the Hamiltonian, i.e., $\rho(q, p, x)$ can be written in the form

$$\rho(\mathbf{q}, \mathbf{p}, x) = \rho(H(\mathbf{q}, \mathbf{p}, x), x), \tag{17}$$

where x is a set of external parameters, and

$$\rho(\mathbf{q}, \mathbf{p}, x) \geq 0, \quad \int \rho(\mathbf{q}, \mathbf{p}, x) d^N \mathbf{q} d^N \mathbf{p} = 1;$$

(2) the distribution function ρ satisfies the Liouville equation

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial \mathbf{q}_i} \left(\frac{\partial H}{\partial \mathbf{p}_i} \rho \right) + \frac{\partial}{\partial \mathbf{p}_i} \left(\left(-\frac{\partial H}{\partial \mathbf{q}_i} + \mathbf{F}_i^{(n)} \right) \rho \right) = 0;$$

(3) the number of particles N is an arbitrary natural number.

Here and later we mean the sum on the repeated index i from 1 to N .

Examples of the thermodynamic few-particle systems:

(1) The constant temperature systems^{1–8} that have the canonical distribution. In general, these systems can be defined by the non-holonomic constraint, which is suggested in Ref. 12.

(2) The classical system with the Breit–Wigner distribution function that is defined by

$$\rho(H(\mathbf{q}, \mathbf{p}, x)) = \frac{\lambda}{(H(\mathbf{q}, \mathbf{p}, x) - E)^2 + (\Gamma/2)^2}. \tag{18}$$

(3) The classical Fermi–Bose canonical-dissipative systems⁹ that are defined by the distribution functions in the form

$$\rho(H(\mathbf{q}, \mathbf{p}, x)) = \frac{1}{\exp[\beta(x)(H(\mathbf{q}, \mathbf{p}, x) - \mu)] + a}. \tag{19}$$

3. Distribution for Thermodynamic Few-Particle Systems

3.1. Formulation of the results

Let us consider the few-particle systems which are defined by the equations

$$\frac{d\mathbf{q}_i}{dt} = \frac{\partial H}{\partial \mathbf{p}_i}, \quad \frac{d\mathbf{p}_i}{dt} = -\frac{\partial H}{\partial \mathbf{q}_i} + \mathbf{F}_i^{(n)}, \tag{20}$$

where $i = 1, \dots, N$. The power of non-potential forces $\mathbf{F}_i^{(n)}$ is defined by

$$\mathcal{P}(\mathbf{q}, \mathbf{p}, x) = \mathbf{F}_i^{(n)} \frac{\partial H}{\partial \mathbf{p}_i}. \tag{21}$$

If the power of the non-potential forces is equal to zero ($\mathcal{P} = 0$) and $\partial H/\partial t = 0$, then few-particle system is called a conservative system. The velocity of an elementary phase volume change Ω is defined by the equation

$$\Omega(\mathbf{q}, \mathbf{p}, x) = \frac{\partial \mathbf{F}_i}{\partial \mathbf{p}_i} + \frac{\partial^2 H}{\partial \mathbf{q}_i \partial \mathbf{p}_i} = \frac{\partial \mathbf{F}_i^{(n)}}{\partial \mathbf{p}_i}. \tag{22}$$

We use the following notations for the scalar product

$$\frac{\partial \mathbf{A}_i}{\partial \mathbf{a}_i} = \sum_{i=1}^N \left(\frac{\partial A_{xi}}{\partial a_{xi}} + \frac{\partial A_{yi}}{\partial a_{yi}} + \frac{\partial A_{zi}}{\partial a_{zi}} \right).$$

The aim of this section is to prove the following result.

Proposition 1. *If the non-potential forces $\mathbf{F}_i^{(n)}$ of the few-particle system (20) satisfy the constraint condition*

$$\frac{\partial \mathbf{F}_i^{(n)}}{\partial \mathbf{p}_i} - \beta(H, x) \mathbf{F}_i^{(n)} \frac{\partial H}{\partial \mathbf{p}_i} = 0, \tag{23}$$

then this system is a thermodynamic few-particle system with the distribution function

$$\rho(\mathbf{q}, \mathbf{p}, x) = \frac{1}{Z(x)} \exp -B(H(\mathbf{q}, \mathbf{p}, x), x), \tag{24}$$

where the function $B(H, x)$ is defined by the equation $\partial B(H, x) / \partial H = \beta(H, x)$, and

$$Z(x) = \int \exp[-B(H(\mathbf{q}, \mathbf{p}, x), x)] d^N \mathbf{q} d^N \mathbf{p}.$$

Obviously, we consider the distribution functions (24) and the function $B = B(H, x)$ such that $\rho \geq 0$, and $Z(x) < \infty$. Note that condition (23) means that the velocity of the elementary phase volume change Ω is directly proportional to the power \mathcal{P} of non-potential forces $\mathbf{F}_i^{(n)}$ of the few-particle system (20) and coefficient of this proportionality is a function $\beta(H, x)$ of Hamiltonian H , i.e.,

$$\Omega(\mathbf{q}, \mathbf{p}, x) - \beta(H, x) \mathcal{P}(\mathbf{q}, \mathbf{p}, x) = 0. \tag{25}$$

Note that any few-particle system with the non-holonomic constraint (25) or (23) is a thermodynamic few-particle system. Solving the Liouville equation with the non-holonomic constraint (23), we can obtain the distributions that are defined by the Hamiltonian.

3.2. Proof of Proposition 1

Let us consider the Liouville equation for the few-particle distribution function $\rho = \rho(\mathbf{q}, \mathbf{p}, x, t)$. This distribution function $\rho(\mathbf{q}, \mathbf{p}, x, t)$ express a probability that a phase space point (\mathbf{q}, \mathbf{p}) will appear. The Liouville equation for this few-particle system

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial \mathbf{q}_i} (\mathbf{K}_i \rho) + \frac{\partial}{\partial \mathbf{p}_i} (\mathbf{F}_i \rho) = 0 \tag{26}$$

expresses the conservation of probability in the phase space. Here we use

$$\mathbf{K}_i = \frac{\partial H}{\partial \mathbf{p}_i}, \quad \mathbf{F}_i = -\frac{\partial H}{\partial \mathbf{q}_i} + \mathbf{F}_i^{(n)}.$$

Using a total time derivative along the phase space trajectory by

$$\frac{d}{dt} = \frac{\partial}{\partial t} + \mathbf{K}_i \frac{\partial}{\partial \mathbf{q}_i} + \mathbf{F}_i \frac{\partial}{\partial \mathbf{p}_i} \tag{27}$$

we can rewrite Eq. (26) in the form

$$\frac{d\rho}{dt} = -\Omega\rho, \quad (28)$$

where the omega function is defined by Eq. (22). In classical mechanics of Hamiltonian systems the right-hand side of the Liouville equation (28) is zero, and the distribution function does not change with time. For the N -particle systems (20), the omega function (22) does not vanish. For this system, the omega function is defined by Eq. (22). For the thermodynamic few-particle systems, this function is defined by the constraint (23) in the form

$$\Omega = \beta(H, x) \mathbf{F}_i^{(n)} \frac{\partial H}{\partial \mathbf{p}_i}. \quad (29)$$

In this case, the Liouville equation has the form

$$\frac{d\rho(\mathbf{q}, \mathbf{p}, x)}{dt} = -\beta(H, x) \mathbf{F}_i^{(n)} \frac{\partial H}{\partial \mathbf{p}_i} \rho. \quad (30)$$

Let us consider the total time derivative of the Hamiltonian. Using equations of motion (20), we have

$$\frac{dH}{dt} = \frac{\partial H}{\partial t} + \frac{\partial H}{\partial \mathbf{p}_i} \frac{\partial H}{\partial \mathbf{q}_i} + \left(-\frac{\partial H}{\partial \mathbf{q}_i} + \mathbf{F}_i^{(n)} \right) \frac{\partial H}{\partial \mathbf{p}_i} = \frac{\partial H}{\partial t} + \mathbf{F}_i^{(n)} \frac{\partial H}{\partial \mathbf{p}_i}. \quad (31)$$

If $\partial H/\partial t = 0$, then the power \mathcal{P} of non-potential forces is equal to the total time derivative of the Hamiltonian

$$\mathbf{F}_i^{(n)} \frac{\partial H}{\partial \mathbf{p}_i} = \frac{dH}{dt}.$$

Therefore Eq. (30) can be written in the form

$$\frac{d \ln \rho(\mathbf{q}, \mathbf{p}, x)}{dt} = -\beta(H, x) \frac{dH}{dt}. \quad (32)$$

If $\beta(H, x)$ is an integrable function, then this function can be represented as a derivative

$$\beta(H, x) = \frac{\partial B(H, x)}{\partial H}. \quad (33)$$

In this case, we can write Eq. (32) in the form

$$\frac{d \ln \rho(\mathbf{q}, \mathbf{p}, x)}{dt} = -\frac{dB(H, x)}{dt}. \quad (34)$$

As a result, we have the following solution of the Liouville equation

$$\rho(\mathbf{q}, \mathbf{p}, x) = \frac{1}{Z(x)} \exp -B(H(\mathbf{q}, \mathbf{p}, x), x). \quad (35)$$

The function $Z(x)$ is defined by the normalization condition. It is easy to see that the distribution function of the N -particle system is determined by the Hamiltonian. Therefore, this system is a thermodynamic few-particle system. Note that N is an arbitrary natural number since we do not use the condition $N \gg 1$ or $N \rightarrow \infty$.

3.3. Few-particle systems with canonical distributions

In this section we consider the thermodynamic few-particle system that is described by canonical distribution.¹² These few-particle systems are defined by the simple function $\beta(H, x) = 3N\beta(x)$ in the non-holonomic constraint (25).

Corollary 1. *If velocity of the elementary phase volume change Ω is directly proportional to the power of non-potential forces \mathcal{P} , then we have the usual canonical Gibbs distribution as a solution of the Liouville equation.*

In other words, the few-particle system with the non-holonomic constraint $\Omega = \beta(x)\mathcal{P}$ can have the canonical Gibbs distribution

$$\rho(\mathbf{q}, \mathbf{p}, x) = \exp \beta(x)(\mathcal{F}(x) - H(\mathbf{q}, \mathbf{p}, x))$$

as a solution of the Liouville equation. Here the coefficient $\beta(x)$ does not depend on $(\mathbf{q}, \mathbf{p}, t)$, i.e., $d\beta(x)/dt = 0$. Proof of this corollary is considered in Ref. 12.

Using Eq. (21), we get the Liouville equation in the form

$$\frac{d\rho(\mathbf{q}, \mathbf{p}, x)}{dt} = -\beta(x)\mathbf{F}_i^{(n)} \frac{\partial H}{\partial \mathbf{p}_i} \rho. \tag{36}$$

The total time derivative for the Hamiltonian is defined by Eq. (31) in the form

$$\frac{dH}{dt} = \frac{\partial H}{\partial t} + \mathbf{F}_i^{(n)} \frac{\partial H}{\partial \mathbf{p}_i}.$$

If $\partial H/\partial t = 0$, then the energy change is equal to the power \mathcal{P} of the non-potential forces $\mathbf{F}_i^{(n)}$. Therefore the Liouville equation can be rewritten in the form

$$\frac{d \ln \rho(\mathbf{q}, \mathbf{p}, x)}{dt} + \beta(x) \frac{dH(\mathbf{q}, \mathbf{p}, x)}{dt} = 0.$$

Since coefficient $\beta(x)$ is a constant ($d\beta(x)/dt = 0$), we have

$$\frac{d}{dt}(\ln \rho(\mathbf{q}, \mathbf{p}, x) + \beta(x)H(\mathbf{q}, \mathbf{p}, x)) = 0,$$

i.e., the value $(\ln \rho + \beta H)$ is a constant along the trajectory of the system in $6N$ -dimensional phase space. Let us denote this constant value by $\beta(x)\mathcal{F}(x)$. Then we have

$$\ln \rho(\mathbf{q}, \mathbf{p}, x) + \beta(x)H(\mathbf{q}, \mathbf{p}, x) = \beta(x)\mathcal{F}(x),$$

where $d\mathcal{F}(x)/dt = 0$. As a result, we get a canonical distribution function

$$\rho(\mathbf{q}, \mathbf{p}, x) = \exp \beta(x)(\mathcal{F}(x) - H(\mathbf{q}, \mathbf{p}, x)).$$

The value $\mathcal{F}(x)$ is defined by the normalization condition. Therefore the distribution of this few-particle system is a canonical distribution.

3.4. Non-canonical distributions for few-particle systems

In Sec 3.3, we consider $\beta(H, x) = \beta(x)$. Let us consider the linear function $\beta = \beta(H, x)$.

Corollary 2. *The linear function $\beta(H, x)$ in the form*

$$\beta(H, x) = \beta_1(x) + \beta_2(x)H$$

leads to the following non-canonical distribution function

$$\rho(\mathbf{q}, \mathbf{p}, x) = \frac{1}{Z(x)} \exp - \left(\beta_1(x)H + \frac{1}{2}\beta_2(x)H^2 \right).$$

The proof of this proposition can be directly derived from Eqs. (35) and (33).

The well known non-Gaussian distribution is the Breit–Wigner distribution. This distribution has a probability density function in the form $\rho(x) = 1/\pi(1+x^2)$. The Breit–Wigner distribution is also known in statistics as Cauchy distribution. The Breit–Wigner distribution is a generalized form originally introduced¹⁸ to describe the cross-section of resonant nuclear scattering in the form

$$\rho(H(\mathbf{q}, \mathbf{p}, x)) = \frac{\lambda}{(H(\mathbf{q}, \mathbf{p}, x) - E)^2 + (\Gamma/2)^2}. \quad (37)$$

This distribution can be derived from the transition probability of a resonant state with known lifetime.^{19–21} The second non-Gaussian distribution, which is considered in this section, is classical Fermi–Bose distribution that was suggested by Ebeling in Refs. 9 and 10. This distribution has the form

$$\rho(H(\mathbf{q}, \mathbf{p}, x)) = \frac{1}{\exp[\beta(x)(H(\mathbf{q}, \mathbf{p}, x) - \mu)] + a}. \quad (38)$$

Corollary 3. *If the function $\beta(H, x)$ of the non-holonomic constrain is defined by*

$$\beta(H, x) = \frac{2(H - E)}{(H - E)^2 + (\Gamma/2)^2}, \quad (39)$$

then we have thermodynamic few-particle systems with the Breit–Wigner distribution (37).

Corollary 4. *If the function $\beta(H, x)$ of the non-holonomic constrain has the form*

$$\beta(H, x) = \frac{\beta(x)}{1 + \alpha \exp \beta(x)H}, \quad (40)$$

then we have thermodynamic few-particle systems with classical Fermi–Bose distribution (38).

Note that Ebeling derives the Fermi–Bose distribution function as a solution of the Fokker–Planck equation. It is known that the Fokker–Planck equation can be derived from the Liouville equation.¹¹ We derive the classical Fermi–Bose distribution as a solution of the Liouville equation.

If the non-potential forces $\mathbf{F}_i^{(n)}$ are determined by the Hamiltonian

$$\mathbf{F}_i^{(n)} = -\partial G(H)/\partial \mathbf{p}_i, \tag{41}$$

then we have the thermodynamic few-particle systems, which are considered in Refs. 9 and 10. These systems are called canonical dissipative systems.

Let us assume that Eq. (17) can be solved in the form

$$H = T(x)G(\rho), \tag{42}$$

where G depends on the distribution ρ . The function $T(x)$ is a function of the parameters x . In this case, the function $\beta(H, x)$ is a composite function

$$C(\rho) = -\beta(T(x)G(\rho), x). \tag{43}$$

This function can be defined by

$$C(\rho) = \frac{1}{\rho} \left(T(x) \frac{\partial G(\rho)}{\partial \rho} \right)^{-1}. \tag{44}$$

As the result, we have the Liouville equation for the few-particle system in the form

$$\frac{d\rho}{dt} = C(\rho)\mathcal{P}. \tag{45}$$

This equation is a nonlinear equation. For example, the classical Fermi-Bose systems⁹ have the function in the form

$$C(\rho) = -\beta(x)(\rho - s\rho_N^2). \tag{46}$$

Note that the nonlinear evolution of statistical systems is considered in Refs. 22–29.

4. Non-Holonomic Constraint

4.1. Formulation of the result

In this section we formulate the proposition, which allows us to derive the thermodynamic few-particle systems from any equation of motion of N -particle systems. The aim of this section is to prove the following result.

Proposition 2. *For any few-particle system, which is defined by the equation*

$$\frac{d\mathbf{q}_i}{dt} = \frac{\partial H}{\partial \mathbf{p}_i}, \quad \frac{d\mathbf{p}_i}{dt} = -\frac{\partial H}{\partial \mathbf{q}_i} + \mathbf{F}_i^{(n)}, \quad i = 1, \dots, N, \tag{47}$$

there exists a thermodynamic few-particle system that is defined by the equations

$$\frac{d\mathbf{q}_i}{dt} = \frac{\partial H}{\partial \mathbf{p}_i}, \quad \frac{d\mathbf{p}_i}{dt} = \mathbf{F}_i^{\text{new}}, \tag{48}$$

and the distribution (24), where the non-potential forces $\mathbf{F}_i^{\text{new}}$ are defined by

$$\mathbf{F}_i^{\text{new}} = \frac{\mathbf{P}_k \mathbf{P}_k \delta_{ij} - \mathbf{P}_i \mathbf{P}_j}{\mathbf{P}_k \mathbf{P}_k} \left(-\frac{\partial H}{\partial \mathbf{q}_j} + \mathbf{F}_j^{(n)} \right) - \frac{\mathbf{P}_i \mathbf{Q}_j}{\mathbf{P}_k \mathbf{P}_k} \frac{\partial H}{\partial \mathbf{p}_j}. \tag{49}$$

The vectors \mathbf{P}_i and \mathbf{Q}_i are defined by the equations

$$\begin{aligned} \mathbf{P}_i = & \frac{\partial\beta(H, x)}{\partial H} \frac{\partial H}{\partial \mathbf{p}_i} \frac{\partial H}{\partial \mathbf{p}_j} \mathbf{F}_j^{(n)} + \beta(H, x) \frac{\partial \mathbf{F}_j^{(n)}}{\partial \mathbf{p}_i} \frac{\partial H}{\partial \mathbf{p}_j} \\ & + \beta(H, x) \mathbf{F}_j^{(n)} \frac{\partial^2 H}{\partial \mathbf{p}_i \partial \mathbf{p}_j} - \frac{\partial^2 \mathbf{F}_j^{(n)}}{\partial \mathbf{p}_i \partial \mathbf{p}_j}, \end{aligned} \quad (50)$$

and

$$\begin{aligned} \mathbf{Q}_i = & \frac{\partial\beta(H, x)}{\partial H} \frac{\partial H}{\partial \mathbf{q}_i} \frac{\partial H}{\partial \mathbf{p}_j} \mathbf{F}_j^{(n)} + \beta(H, x) \frac{\partial \mathbf{F}_j^{(n)}}{\partial \mathbf{q}_i} \frac{\partial H}{\partial \mathbf{p}_j} \\ & + \beta(H, x) \mathbf{F}_j^{(n)} \frac{\partial^2 H}{\partial \mathbf{q}_i \partial \mathbf{p}_j} - \frac{\partial^2 \mathbf{F}_j^{(n)}}{\partial \mathbf{q}_i \partial \mathbf{p}_j}. \end{aligned} \quad (51)$$

Here we use the following notations

$$\mathbf{a}_i \mathbf{b}_j \mathbf{c}_j = \mathbf{a}_i \sum_{j=1}^N (b_{xj} c_{xj} + b_{yj} c_{yj} + b_{zj} c_{zj}).$$

Note that the forces that are defined by Eqs. (49), (50) and (51) satisfy the non-holonomic constraint (25), i.e.,

$$\frac{\partial \mathbf{F}_j^{\text{new}}}{\partial \mathbf{p}_j} + \frac{\partial^2 H}{\partial \mathbf{q}_j \partial \mathbf{p}_j} - \beta(H, x) \mathbf{F}_j^{\text{new}} \frac{\partial H}{\partial \mathbf{p}_j} = 0, \quad (52)$$

where we use the omega function in the form (22).

4.2. Proof of Proposition 2

Let us prove Eq. (49). Let us consider the N -particle classical system in the Hamilton picture. Denote the position of the i th particle by \mathbf{q}_i and its momentum by \mathbf{p}_i . Suppose that the system is subjected to a non-holonomic (non-integrable) constraint in the form

$$f(\mathbf{q}, \mathbf{p}, x) = 0. \quad (53)$$

Differentiation of Eq. (53) with respect to time gives a relation

$$\mathbf{P}_i(\mathbf{q}, \mathbf{p}, x) \frac{d\mathbf{p}_i}{dt} + \mathbf{Q}_i(\mathbf{q}, \mathbf{p}, x) \frac{d\mathbf{r}_i}{dt} = 0, \quad (54)$$

where the functions \mathbf{P}_i and \mathbf{Q}_i are defined by the equations

$$\mathbf{P}_i(\mathbf{q}, \mathbf{p}, x) = \frac{\partial f}{\partial \mathbf{p}_i}, \quad \mathbf{Q}_i(\mathbf{q}, \mathbf{p}, x) = \frac{\partial f}{\partial \mathbf{q}_i}. \quad (55)$$

An unconstrained motion of the i th particle, where $i = 1, \dots, N$, is described by the equations

$$\frac{d\mathbf{q}_i}{dt} = \mathbf{K}_i, \quad \frac{d\mathbf{p}_i}{dt} = \mathbf{F}_i, \quad (56)$$

where \mathbf{F}_i is a resulting force, which acts on the i th particle.

The unconstrained motion gives a trajectory which leaves the constraint hypersurface (53). The constraint forces \mathbf{R}_i must be added to the equation of motion to prevent the deviation from the constraint hypersurface:

$$\frac{d\mathbf{q}_i}{dt} = \mathbf{K}_i, \quad \frac{d\mathbf{p}_i}{dt} = \mathbf{F}_i + \mathbf{R}_i. \tag{57}$$

The constraint force \mathbf{R}_i for the non-holonomic constraint is proportional to the \mathbf{P}_i :³⁰

$$\mathbf{R}_i = \lambda \mathbf{P}_i, \tag{58}$$

where the coefficient λ of the constraint force term is an undetermined Lagrangian multiplier. For the non-holonomic constraint (53), the equations of motion (56) are modified as

$$\frac{d\mathbf{q}_i}{dt} = \mathbf{K}_i, \quad \frac{d\mathbf{p}_i}{dt} = \mathbf{F}_i + \lambda \mathbf{P}_i. \tag{59}$$

The Lagrangian coefficient λ is determined by Eq. (54). Substituting Eq. (57) into Eq. (54), we get

$$\mathbf{P}_i(\mathbf{F}_i + \lambda \mathbf{P}_i) + \mathbf{Q}_i \mathbf{K}_i = 0. \tag{60}$$

Therefore the Lagrange multiplier λ is equal to

$$\lambda = -\frac{\mathbf{P}_i \mathbf{F}_i + \mathbf{Q}_i \mathbf{K}_i}{\mathbf{P}_k \mathbf{P}_k}. \tag{61}$$

As a result, we obtain the following equations

$$\frac{d\mathbf{q}_i}{dt} = \mathbf{K}_i, \quad \frac{d\mathbf{p}_i}{dt} = \mathbf{F}_i - \mathbf{P}_i \frac{\mathbf{P}_j \mathbf{F}_j + \mathbf{Q}_j \mathbf{K}_j}{\mathbf{P}_k \mathbf{P}_k}. \tag{62}$$

These equations we can rewrite in the form (56)

$$\frac{d\mathbf{q}_i}{dt} = \mathbf{K}_i, \quad \frac{d\mathbf{p}_i}{dt} = \mathbf{F}_i^{\text{new}} \tag{63}$$

with the new forces

$$\mathbf{F}_i^{\text{new}} = \frac{\mathbf{P}_k \mathbf{P}_k \delta_{ij} - \mathbf{P}_i \mathbf{P}_j}{\mathbf{P}_k \mathbf{P}_k} \mathbf{F}_j - \frac{\mathbf{P}_i \mathbf{Q}_j}{\mathbf{P}_k \mathbf{P}_k} \mathbf{K}_j. \tag{64}$$

In general, the forces $\mathbf{F}_i^{\text{new}}$ are non-potentials forces (see examples in Ref. 12).

Equation (62) are equations of the *holonomic* system. For any trajectory of the system in the phase space, we have $f = \text{const}$. If initial values $\mathbf{q}_k(0)$ and $\mathbf{p}_k(0)$ satisfy the constraint condition $f(\mathbf{q}(0), \mathbf{p}(0), x) = 0$, then solution of Eqs. (62) and (64) is a motion of the non-holonomic system.

Let us prove Eqs. (50) and (51). In order to prove these equations, we consider the few-particle system (56) with

$$\mathbf{K}_i = \frac{\partial H}{\partial \mathbf{p}_i}, \quad \mathbf{F}_i = -\frac{\partial H}{\partial \mathbf{q}_i} + \mathbf{F}_i^{(n)}, \tag{65}$$

and the special form of the non-holonomic constraint (53). Let us assume the following constraint: the velocity of the elementary phase volume change $\Omega(\mathbf{q}, \mathbf{p}, x)$ is directly proportional to the power $\mathcal{P}(\mathbf{q}, \mathbf{p}, x)$ of the non-potential forces, i.e.,

$$\Omega(\mathbf{q}, \mathbf{p}, x) = \beta(H, x)\mathcal{P}(\mathbf{q}, \mathbf{p}, x), \tag{66}$$

where $\beta(H, x)$ depends on the Hamiltonian H . Therefore the system is subjected to a non-holonomic (non-integrable) constraint (53) in the form

$$f(\mathbf{q}, \mathbf{p}, x) = \beta(H, x)\mathcal{P}(\mathbf{q}, \mathbf{p}, x) - \Omega(\mathbf{q}, \mathbf{p}, x) = 0. \tag{67}$$

This constraint is a generalization of the condition which is suggested in Ref. 12. The power \mathcal{P} of the non-potential forces $\mathbf{F}_i^{(n)}$ is defined by Eq. (21). The function Ω is defined by Eq. (22). As the result, we have Eq. (67) for the non-potential forces in the form

$$\beta(H, x)\mathbf{F}_j^{(n)} \frac{\partial H}{\partial \mathbf{p}_j} - \frac{\partial \mathbf{F}_j^{(n)}}{\partial \mathbf{p}_j} = 0.$$

The functions \mathbf{P}_i and \mathbf{Q}_i for this constraint can be find by differentiation of constraint. Differentiation of the function $f(\mathbf{q}, \mathbf{p}, x)$ with respect to \mathbf{p}_i gives

$$\mathbf{P}_i(\mathbf{q}, \mathbf{p}, x) = \frac{\partial f}{\partial \mathbf{p}_i} = \frac{\partial}{\partial \mathbf{p}_i} \left(\beta(H, x)\mathbf{F}_j^{(n)} \frac{\partial H}{\partial \mathbf{p}_j} \right) - \frac{\partial}{\partial \mathbf{p}_i} \frac{\partial \mathbf{F}_j^{(n)}}{\partial \mathbf{p}_j}.$$

This expression leads us to Eq. (50). Differentiation of the function $f(\mathbf{q}, \mathbf{p}, t)$ with respect to \mathbf{q}_i gives

$$\mathbf{Q}_i(\mathbf{q}, \mathbf{p}, x) = \frac{\partial f}{\partial \mathbf{q}_i} = \frac{\partial}{\partial \mathbf{q}_i} \left(\beta(H, x)\mathbf{F}_j^{(n)} \frac{\partial H}{\partial \mathbf{p}_j} \right) - \frac{\partial}{\partial \mathbf{q}_i} \frac{\partial \mathbf{F}_j^{(n)}}{\partial \mathbf{p}_j}.$$

This expression leads to Eq. (51).

4.3. Few-particle systems with minimal constraint

Let us consider the simple constraints for to realize the classical systems with canonical and non-canonical distributions. Let us consider few-particle system which are defined by the simplest form of the Hamiltonian

$$H(\mathbf{q}, \mathbf{p}, x) = \frac{\mathbf{p}^2}{2m} + U(\mathbf{q}, x), \tag{68}$$

and the non-potential forces

$$\mathbf{F}_i^{(n)} = -\gamma \mathbf{p}_i, \tag{69}$$

Here $\mathbf{p}^2 = \sum_{i=1}^N \mathbf{p}_i^2$, and N is a number of particles. For the minimal constraint models, the non-holonomic constraint is defined by the equation

$$f(\mathbf{q}, \mathbf{p}, x) = \beta(H, x) \frac{\mathbf{p}^2}{m} - 3N = 0, \tag{70}$$

The phase space gradients (50) and (51) of this constraint are represented in the form

$$\mathbf{P}_i = \left(\frac{\partial\beta(H, x)}{\partial H} \frac{\mathbf{p}^2}{2m} + \beta(H, x) \right) \frac{2\mathbf{p}_i}{m}, \quad \mathbf{Q}_i = \frac{\partial\beta(H, x)}{\partial H} \frac{\partial H}{\partial \mathbf{q}_i}.$$

The non-potential forces of the minimal constraint models have the form

$$\mathbf{F}_i^{\text{new}} = -\frac{\mathbf{p}^2\delta_{ij} - \mathbf{p}_i\mathbf{p}_j}{\mathbf{p}^2} \frac{\partial U}{\partial \mathbf{q}_j} + \frac{\mathbf{p}_i\mathbf{p}_j}{2\mathbf{p}^2((\mathbf{p}^2/2m)\partial\beta(H, x)/\partial H) + \beta(H, x)} \frac{\partial\beta(H, x)}{\partial H} \frac{\partial U}{\partial \mathbf{q}_j}.$$

It is easy to see that all minimal constraint models have the potential forces.

Note that the minimal Gaussian constraint model is characterized by

$$\frac{\partial\beta(H, x)}{\partial H} = 0.$$

In this case, we have the non-potential forces in the form

$$\mathbf{F}_i^{\text{new}} = -\frac{\mathbf{p}^2\delta_{ij} - \mathbf{p}_i\mathbf{p}_j}{\mathbf{p}^2} \frac{\partial U}{\partial \mathbf{q}_j}.$$

The few-particle systems are the constant temperature systems that are considered in Refs. 1–8 and 12.

4.4. Few-particle systems with minimal gaussian constraint

Let us consider the N -particle system with the Hamiltonian (68), the function $\beta(H, x) = 3N/kT(x)$, and the linear friction force (69). Substituting Eq. (69) into Eqs. (21) and (22), we get the power \mathcal{P} and the omega function Ω :

$$\mathcal{P} = -\frac{\gamma}{m}\mathbf{p}^2, \quad \Omega = -3\gamma N.$$

In this case, the non-holonomic constraint has the form

$$\frac{\mathbf{p}^2}{m} = kT(x), \tag{71}$$

i.e., the kinetic energy of the system must be a constant. Note that Eq. (71) has not the friction parameter γ .

For the few-particle system with friction (69) and non-holonomic constraint (71), we have the following equations of motion

$$\frac{d\mathbf{q}_i}{dt} = \frac{\mathbf{p}_i}{m}, \quad \frac{d\mathbf{p}_i}{dt} = -\frac{\partial U}{\partial \mathbf{q}_i} - \gamma\mathbf{p}_i + \lambda \frac{\partial f}{\partial \mathbf{p}_i}, \tag{72}$$

where the function $f = f(\mathbf{q}, \mathbf{p})$ is defined by

$$f(\mathbf{q}, \mathbf{p}) = \frac{1}{2}(\mathbf{p}^2 - mkT(x)) : f(\mathbf{q}, \mathbf{p}) = 0. \tag{73}$$

Equation (72) and condition (73) define $6N + 1$ variables $(\mathbf{q}, \mathbf{p}, \lambda)$. Let us find the Lagrange multiplier λ . Substituting Eq. (73) into Eq. (72), we get

$$\frac{d\mathbf{p}_i}{dt} = -\frac{\partial U}{\partial \mathbf{q}_i} + (\lambda - \gamma)\mathbf{p}_i. \tag{74}$$

Using $df/dt = 0$ in the form

$$\mathbf{p}_i \frac{d\mathbf{p}_i}{dt} = 0 \tag{75}$$

and substituting Eq. (74) into Eq. (75), we get the Lagrange multiplier λ in the form

$$\lambda = \frac{1}{mkT(x)} \mathbf{p}_j \frac{\partial U}{\partial \mathbf{q}_j} + \gamma.$$

As a result, we have the holonomic system that is defined by the equations

$$\frac{d\mathbf{q}_i}{dt} = \frac{\mathbf{p}_i}{m}, \quad \frac{d\mathbf{p}_i}{dt} = \frac{1}{mkT(x)} \mathbf{p}_i \mathbf{p}_j \frac{\partial U}{\partial \mathbf{q}_j} - \frac{\partial U}{\partial \mathbf{q}_i}. \tag{76}$$

For the few-particle system (76), condition (71) is satisfied. If the time evolution of the few-particle system is defined by Eq. (76), then we have the canonical distribution function in the form

$$\rho(\mathbf{q}, \mathbf{p}, x) = \frac{1}{Z(x)} \exp -\frac{H(\mathbf{q}, \mathbf{p}, x)}{kT(x)}. \tag{77}$$

where $Z(x)$ is defined by the normalization condition. For example, the few-particle system with the forces

$$\mathbf{F}_i = -m\omega^2(x)\mathbf{q}_i + \frac{\omega^2(x)}{kT(x)} \mathbf{p}_i (\mathbf{p}_j \mathbf{q}_j) \tag{78}$$

has canonical distribution (77) of the linear harmonic oscillator with Hamiltonian

$$H(\mathbf{q}, \mathbf{p}, x) = \frac{\mathbf{p}^2}{2m} + \frac{m\omega^2(x)\mathbf{q}^2}{2}.$$

5. Conclusion

In this paper we derive the extension of the statistical thermodynamics to the wide class of few-particle systems. We consider few-particle systems with distributions that are defined by Hamiltonian and Liouville equation. These systems are described by the non-holonomic (non-integrable) constraint:¹² the velocity of the elementary phase volume change is directly proportional to the power of non-potential forces. In the general case, the coefficient of this proportionality is defined by the Hamiltonian. This constraint allows us to derive the distribution function of the few-particle system, even in far-from equilibrium states. The few-particle systems that have some analog of the thermodynamic laws is characterized by the distribution functions that are determined by the Hamiltonian. The examples of these few-particle systems are the constant temperature systems,¹⁻⁸ the canonical-dissipative systems,^{9,10} and the

Fermi–Bose classical systems.⁹ For the few-particle systems, we can use the analogs of the usual thermodynamics laws. Note that the number of particles is an arbitrary natural number since we do not use the condition $N \gg 1$ or $N \rightarrow \infty$. This allows one to use the suggested few-particle systems for the simulation¹⁷ for the molecular dynamics.

The quantization of the evolution equations for non-Hamiltonian and dissipative systems was suggested in Refs. 31 and 32. Using this quantization it is easy to derive the quantum analog of few-particle systems that leads to some analog of the thermodynamic laws. We can derive the canonical and non-canonical statistical operators³³ that are determined by the Hamiltonian.^{13,14} The suggested few-particle systems can be generalized by the quantization method that is considered in Refs. 31 and 32.

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