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METHODOLOGICAL NOTES

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On the problem of thermodynamic fluctuations in computer simulations

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Contents

Abstract. **We discuss two approaches to studying thermodynamic fluctuations in computer simulations. The first is based on the theory presented in Landau and Lifshitz's textbook, which assumes a self-consistent solution to the problem, and the second, developed by Lebowitz–Percus–Verlet, et al., is suitable for a limited class of computer simulations based on the classical method of molecular dynamics. The study of fluctuations in a molecular dynamics simulation of helium fluid at room temperature and a pressure of 2 kbar reveals that they differ by several times depending on the type of ensemble (NVE or NVT) used in the computations. For the NVT ensemble, the best result is given by the Landau–Lifshitz approach, and for the microcanonical NVE ensemble, by the Lebowitz–Percus–Verlet approach. At the same time, the NVT ensemble in this system is shown to have a distribution density of temperature fluctuations different from the normal one. This difference is associated with the presence of so-called algorithmic fluctuations caused by the computer implementation of the calculation algorithm: discreteness of time, limited computation time, etc. The fundamental possibility of reconciling the weakly conservative laws of particle motion, where energy is conserved on average, with the manifest asymmetry of the time evolution of the system as a whole is demonstrated.**

Keywords: thermodynamic fluctuations, molecular dynamics, bulk moduli, specific heat

1. Introduction

Thermodynamic fluctuations are an intrinsic feature of statistical mechanics, dating back to the foundational course on theoretical physics by Landau and Lifshitz [1]. Although the idea of fluctuations of thermodynamic quantities (such as temperature) was initially opposed by physicists (for more details, see [2–5]), fluctuations of some thermodynamic properties are used to derive various thermodynamic quantities (such as isochoric heat capacity and adiabatic elastic modulus) in molecular dynamics calculations [6–9]. In such calculations, different approaches are used, providing different final values of thermodynamic parameters: canonical (in the thermodynamic sense) in accordance with the course on theoretical physics by Landau and Lifshitz [1], and microcanonical in accordance with the approach of Lebowitz–Percus–Verlet et al. [10, 11]. The difference between the two approaches (the first one is claimed to be applicable to a real physical system, and the second, to computer molecular dynamics simulations) is manifested in the magnitude of thermodynamic fluctuations of an ideal Boltzmann gas, for which the second approach predicts the absence of fluctuations of thermodynamic parameters, in contrast to the first one. In addition, as we show below, the approach in Landau and Lifshitz's textbook [1] provides a self-consistent system of thermodynamic equalities that can be used to interpret fluctuations in real experiments or computer simulations.

We emphasize that, by thermodynamic fluctuations, we mean irregular oscillations of thermodynamic quantities (temperature T, volume V, entropy S, and pressure P) that can be related to certain thermodynamic characteristics of a sample (such as the heat capacity, elastic modulus, and thermal expansion coefficient). In this way, they differ from, so to speak, kinetic fluctuations (similar to those observed in the Brownian motion of small particles), associated, according to Kubo's formula [12], with a certain kinetic coefficient. For example, the Brownian motion of small particles, according to the Einstein–Smoluchowski formula, is associated with the diffusion coefficient and viscosity. Generally speaking, thermodynamic fluctuations remain an ongoing problem that has caused intense debate in the past (see the discussion of the famous physicists Kittel and Mandelbrot

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about temperature fluctuations [4, 5]), because they have not yet received experimental confirmation. Kittel believed that the temperature is set by the temperature of the thermostat. Because the thermostat can be made arbitrarily large, and the temperature fluctuations behave as $1/\sqrt{N}$ (where N is the number of particles in the system), it follows that there are no temperature fluctuations in any volume, no matter how small.

This dispute goes back to the classic works of Gibbs and Einstein [13–15] and concerns the fundamental principles of statistical physics. The concept of thermodynamic fluctuations was first introduced by Gibbs in his classic study [13], but, in his approach to statistical physics, temperature is a fixed parameter that cannot fluctuate. Einstein's approach, developed in Landau and Lifshitz's textbook [14, 15], was formulated in a 1910 paper and allowed any thermodynamic parameter, including temperature, to fluctuate. However, as was shown much later in [16], Gibbs's work contains prerequisites for Einstein's approach, and hence the two standpoints can be reconciled, which can be achieved by studying fluctuations of the cosmic microwave background.

Perhaps modern thermodynamic studies of nanoobjects, where thermodynamic fluctuations are most pronounced but also much more difficult to register than in macroscopic objects, will help to resolve this problem. At the same time, thermodynamic fluctuations can be observed practically 'for free' in computer simulations.

2. Implications of theory of thermodynamic fluctuations

The root-mean-square fluctuations of thermodynamic quantities Δx (for $x = T, V, S, P$) are given in the table. Although this table is well known from the exercises given in Landau and Lifshitz's textbook [1], in such a compact form (as a multiplication table) it was compiled in Wikipedia [17]. It follows from the table that there are certain correlations between different fluctuations of thermodynamic parameters. It can be easily found that such correlations are provided by two linear equations for fluctuations:

$$T\Delta S = C_V \Delta T + T\left(\frac{\partial P}{\partial T}\right)_V \Delta V, \tag{1}$$

$$\Delta P = \left(\frac{\partial P}{\partial T}\right)_V \Delta T + \left(\frac{\partial P}{\partial V}\right)_T \Delta V. \tag{2}$$

Both equations can be regarded as definitions of the fluctuations of entropy and pressure. In this capacity, they were first presented in Landau and Lifshitz's book [1]. As regards the last equation, a minor clarification is required. If we restrict ourselves to classical molecular dynamics modeling, then calculating the instantaneous values of temperature (based on the kinetic energy) and pressure (based on the virial formula) is a simple task. On the other hand, there is no simple way to calculate the instantaneous values of volume and entropy. Pressure and temperature are intensive thermodynamic variables (independent of the number of particles), while volume and entropy are extensive variables, proportional to the number of particles, if we do not consider the effects of surfaces and phase boundaries in small systems. In the second case, the situation becomes even more complicated when we consider a small volume in a dynamical system of interacting particles (as was done when considering thermodynamic fluctuations in Landau and Lifshitz's book), and therefore it is not even quite clear what is meant by fluctuations of this small volume. Thus, the formulas given above can be regarded as *definitions* of fluctuations in volume and entropy.

Table. Average value $\langle x_i x_j \rangle$ ($x_{i,j} = \Delta T, \Delta V, \Delta S, \Delta P$) of thermodynamic fluctuations according to course on theoretical physics by Landau and Lifshitz [1]. C_P and C_V are isobaric and isothermal heat capacity of sample, respectively.

	ΔT	ΔV	ΔS	ΔP
ΔT	$\frac{k_B}{C_V} T^2$	0	$k_B T$	$\frac{k_B}{C_V} T^2 \left(\frac{\partial P}{\partial T}\right)_V$
ΔV	·	$-k_B T \left(\frac{\partial V}{\partial P}\right)_T$	$k_B T \left(\frac{\partial V}{\partial T}\right)_P$	$-k_B T$
ΔS	·	·	$k_B C_P$	0
ΔV	·	·	·	$-k_B T \left(\frac{\partial P}{\partial V}\right)_S$

It can be shown that both formulas are exact, i.e., they lead to a detailed balance of fluctuations, and hence both equations are satisfied at any time instant.

By calculating the second moment of both equations (by taking the square of both sides of the equations and calculating its average value in accordance with the table), it can be demonstrated that it is exactly zero. This can be proved easily using the thermodynamic identities

$$-V\left(\frac{\partial P}{\partial V}\right)_{S,T} = B_{S,T}\,, \quad \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \alpha\,, \quad \left(\frac{\partial P}{\partial T}\right)_V = \alpha B_T\,,$$

$$\frac{B_S - B_T}{B_T} = \frac{\alpha^2 B_T T V}{C_V} = \alpha \chi T = \frac{C_P - C_V}{C_V}\,,$$

where α is the coefficient of volumetric thermal expansion, $B_{S,T}$ are adiabatic and isothermal volumetric moduli, and χ is the Grüneisen coefficient.

However, the first equation can be viewed from another angle, as a form of the energy conservation equation

$$\Delta Q = \Delta E + \Delta A\,, \tag{3}$$

where heat fluctuations

$$\Delta Q = T\Delta S \tag{4}$$

are caused by fluctuations in the internal energy

$$\Delta E = C_V \Delta T + \left(T\left(\frac{\partial P}{\partial T}\right)_V - P\right)\Delta V \tag{5}$$

and work against internal volume fluctuations:

$$\Delta A = P\Delta V\,. \tag{6}$$

The energy balance is exact, and therefore energy is conserved at every instant of time. At first glance, it may seem that the energy balance allows a stationary solution with all mean values of the oscillations vanishing: $\langle \Delta Q \rangle = \langle \Delta A \rangle = \langle \Delta E \rangle = 0$. But we demonstrate that this is impossible.

We must admit that the condition $\langle \Delta E \rangle = 0$ is in principle possible, because the internal energy balance is governed by mechanical laws that are conservative.

However, such an energy balance is not exact, as can be shown by calculating the second moment of the internal energy fluctuations,

$$\langle \Delta E^2 \rangle = -k_{\mathrm{B}} \left(T \left(\frac{\partial P}{\partial T} \right)_V - P \right)^2 T \left(\frac{\partial V}{\partial P} \right)_T + k_{\mathrm{B}} C_V T^2 , \quad (7)$$

which cannot be reduced to thermodynamic identities. This means that, while $\langle \Delta E \rangle = 0$, $\langle \Delta E^2 \rangle \neq 0$. We call such systems weakly conservative. We now suppose that $\langle \Delta S \rangle = 0$ (i.e., the process is reversible) or $\langle \Delta Q \rangle = 0$, namely, the exact opposite to what we set out to prove. Because entropy is assumed to be conserved, it follows from the second law of thermodynamics that the efficiency of the thermodynamic fluctuations is equal to the Carnot cycle efficiency $\eta = \Delta T / T$, whence we derive the equation $\Delta A = \Delta Q \eta = \Delta S \Delta T$ for work. Next, averaging Eqn (3) and referring to the table, we arrive at the equality $\langle \Delta S \Delta T \rangle + \langle \Delta E \rangle = k_{\mathrm{B}} T = \langle T \Delta S \rangle$. For a time interval when the temperature T changes insignificantly, we can conclude that $k_{\mathrm{B}} = \langle \Delta S \rangle$, which contradicts our initial assumption. Therefore, we have proved that entropy cannot be conserved on average during fluctuations. In fact, this conclusion is almost obvious: the fluctuations strongly differ from those in the Carnot cycle and cannot be reduced to a finite number of Carnot cycles, and are therefore essentially not isentropic. At the same time, such a simple and clear proof that dissipation (i.e., irreversibility) follows from fluctuations is, in all likelihood, presented here for the first time.

What is the source of fluctuations? In other words, what is the reason for dynamical systems being weakly conservative? If we take computer implementations of real dynamical systems, then the answer most likely lies in the discreteness of the integration time of differential equations, i.e., in any computer experiment that obeys strictly conservative laws of motion, we are apparently dealing with a weakly conservative system [18]. At the same time, in real experiments, the source of irreversibility can be, for example, the processes of absorption and emission of photons [19].

As an example, we consider ideal and almost ideal (van der Waals) gases. What happens when a flask with such a gas breaks in a vacuum? The gas certainly begins to expand, but what happens to its temperature? For an ideal gas, the answer is almost obvious, because the interaction between gas molecules is zero, and hence, as the gas expands, the kinetic energy does not change, and therefore the temperature does not change either. This can also be shown from the equation for the fluctuations of the internal energy: for an ideal gas, the dependence $P(V, T)$ is linear in T, and therefore internal energy fluctuations due to volume fluctuations are zero; hence, in order to keep the internal energy equal to zero on average, its part due to temperature fluctuations must also be zero. Therefore, the temperature does not change. On the other hand, the volume and entropy of an ideal gas tend to infinity during infinite expansion. For a nearly ideal van der Waals gas, the conclusion about the constancy of the gas temperature during expansion is not valid. Although $P(V, T)$ of a van der Waals gas also depends linearly on T, a constant term a/V^2 is then involved in the formula for the internal energy fluctuations $\Delta E = a \Delta V / V^2 + C_V \Delta T$. When the gas expands, for the internal energy fluctuations to be conserved on average, the term dependent on the volume fluctuations must be compensated by temperature fluctuations, and hence the expansion of the gas must be accompanied by a decrease in its temperature. In that case, the conclusion is also largely obvious, because overcoming the attraction of gas molecules must be accompanied by a decrease in their kinetic energy, which results in the gas cooling.

We have demonstrated how the conservation of energy in the dynamics of a system governed by weakly conservative laws of particle motion can be reconciled with the apparent asymmetry of the time evolution of the system as a whole. Although the internal energy may be conserved on average during the time evolution of a classical dynamical system, the overall evolution of entropy and volume is not stationary during fluctuations, and hence the average fluctuations of volume and entropy are not zero. In our opinion, this is because of the lack of a computationally feasible procedure that would yield instantaneous values of entropy and volume in a fluctuating system, and therefore such fluctuations can only be obtained from instantaneous values of pressure and temperature.

It may seem that these difficulties can be bypassed by developing a procedure for calculating fluctuations with the volume kept strictly constant, thereby simulating molecular dynamics calculations in NVE ensembles. This was attempted in the above-mentioned Lebowitz–Percus–Verlet study [10] in terms of the microcanonical ensemble. For the mean square temperature fluctuations (which can be obtained from the formulas for kinetic energy fluctuations given in [11]), the following formula holds:

$$\Delta T^2 = \frac{2T^2}{3N} \left(1 - \frac{3 k_{\mathrm{B}} N}{2 C_V} \right) . \quad (8)$$

The formulas for $\langle \Delta P^2 \rangle$ and $\langle \Delta P \Delta T \rangle$ are more complicated, and we do not quote them here (they can be found in the same paper [11]), but formula (8) is remarkable in that, for a monatomic ideal gas with $C_V = (3/2) N k_{\mathrm{B}}$, it obviously predicts the absence of temperature fluctuations. In principle, this is a verifiable statement. Although it is impossible to simulate the ideal gas in a computer experiment, it is possible to take a system close enough to an ideal gas, with a heat capacity close to $3 k_{\mathrm{B}} N/2$. Such a system can be helium at room temperature and a pressure of 2 kbar.

3. Fluctuations in helium fluid at $T = 298$ K and $P = 0.2$ GPa

We use the data presented in [20], where the simulation of a helium–argon mixture was compared with previously obtained experimental data. One of the limiting points — pure helium — was simulated using the Lennard-Jones potential with parameters adjusted to the simulated system (argon–helium mixture) in order to obtain agreement between the theoretical and experimental results. The computer experiment was performed using the popular molecular dynamics package LAMMPS [21, 22]. The simulation was performed in an NVT ensemble with a Nosé–Hoover thermostat in a system consisting of 32,000 atoms. The time step was 1 fs, and data were collected over 50×10^6 steps with a periodicity of 500 steps. It was found that the specific heat capacity (which agrees well with the experimental value) is $\approx 1.65 k_{\mathrm{B}}$ per atom, and hence the system is quite close to an ideal gas. It is easy to verify that the temperature fluctuations for such a system, obtained from the table (according to Landau–Lifshitz [1]) and formula (8) (according to Lebowitz–Percus–Verlet [10]), differ by almost 15 times (the second value being smaller).

Informally speaking, we used LAMMPS in the black box regime: the initial data (the number of particles, the cell volume, the required temperature, the integration step, and the coordinates and velocities of particles) were fed to the input, and the instantaneous temperature, pressure, and internal energy were obtained at the output. LAMMPS is actually a standard in molecular dynamics, especially because it is an open source package, and we therefore believe that it computes all parameters correctly (at least inasmuch as is possible in molecular dynamics). It computes the temperature from the average kinetic energy (according to the equipartition law) and the pressure, from the virial formula, which means that the temperature here is actually the kinetic energy of all particles in the computational cell (volume). All output values (including internal energy) fluctuate around equilibrium values. What happens if we use the NVE ensemble instead of the NVT one? This does not change anything in principle: the internal energy fluctuates in the NVE ensemble as well (just as the temperature fluctuates in the NVT ensemble), but the relative energy fluctuations are significantly smaller in the NVE ensemble ($\Delta E/E \approx 10^{-6}$) than in the NVT ensemble ($\Delta E/E \approx 10^{-2}$). It is for this reason that the Lebowitz–Percus–Verlet approach can be used to analyze temperature fluctuations in the first case.

To compare the data obtained in the computer simulation with theoretical predictions, it is necessary to know several values of the derivatives of thermodynamic quantities, which requires calculating the internal energy and pressure along an isochore and an isotherm in the vicinity of the point under study, after which the finite-difference differentiation procedure is used to obtain estimates of the required derivatives. Although the values are calculated along the isotherm and isochore, the isobaric and adiabatic values of the parameters (used for the theoretical estimation of the magnitude of fluctuations) can be obtained using the thermodynamic identity mentioned earlier:

$$\frac{B_S - B_T}{B_T} = \frac{C_P - C_V}{C_V} = \frac{(\partial P/\partial T)_V^2 TV}{C_V B_T}\,. \tag{9}$$

The procedure for calculating the derivatives of the thermodynamic parameters is illustrated in Fig. 1, which also shows an estimate of the standard deviations of the internal energy, temperature, and pressure obtained in the simulations. From the graphs provided, we can estimate $(\partial P/\partial T)_V$, $(\partial E/\partial T)_V$, and $(\partial P/\partial V)_T$. The approximate equality of the derivative $(\partial E/\partial V)_T$ to zero also illustrates the closeness of the system under consideration to an ideal gas.

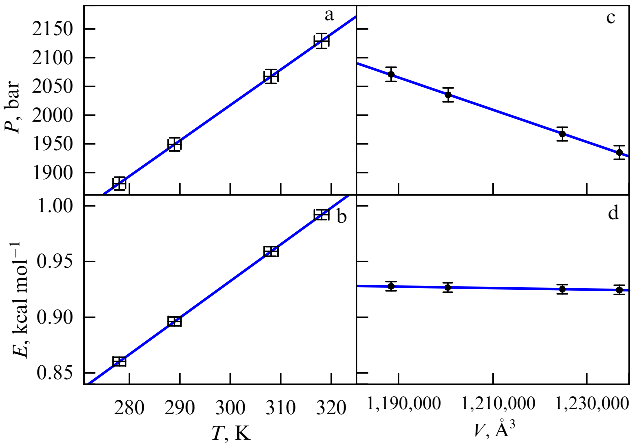

Figure 1. Calculation of derivatives of thermodynamic quantities (a) $(\partial P/\partial T)_V$, (b) $(\partial E/\partial T)_V$ (at fixed $V = 1188$ nm^3), (c) $(\partial P/\partial V)_T$, and (d) $(\partial E/\partial V)_T$ (at fixed $T = 298$ K) in gaseous helium near $T = 298$ K and $P = 0.2$ GPa.

We present the values of thermodynamic fluctuations obtained in the simulation in the NVT ensemble, and (in parentheses) the predicted values according to Landau–Lifshitz: $\langle \Delta T^2 \rangle = 1.75$ (1.67 ± 0.1) K^2, $\langle \Delta P^2 \rangle = 150$ (179 ± 10) bar^2, and $\langle \Delta T \Delta P \rangle = 6.5$ (10 ± 1) bar K. In all three cases, the theoretical predictions are seen to approximately correspond to the fluctuation values observed in simulations. In the NVE ensemble, the simulations yield $\langle \Delta T^2 \rangle = 0.18$ K^2, which is significantly less than in the NVT ensemble but nevertheless 1.5 times greater than follows from formula (8). This observation also implies the need to take into account volume fluctuations for the correct calculation of internal energy fluctuations in NVT/NVE ensembles.

The problem of thermodynamic fluctuations in the NVT ensemble, where the volume is considered a fixed value, was considered in [23]. For the $\langle \Delta T^2 \rangle$ and $\langle \Delta T \Delta P \rangle$ fluctuations, the obtained values coincide with the results of the Landau–Lifshitz approach (which in [23] was considered to be equivalent to the problem of thermodynamic fluctuations in the NPT ensemble), but the following formula was obtained for pressure fluctuations:

$$\langle \Delta P^2 \rangle = \frac{k_B T^2}{C_V} \left(\frac{\partial P}{\partial T} \right)_V^2 . \tag{10}$$

It is easy to see that, in our case, this formula gives significantly underestimated values: $\langle \Delta P^2 \rangle = 64$ bar^2. This also indicates that the nominally fixed volume in NVT calculations is also subject to fluctuations.

When estimating internal energy fluctuations, a 'truncated' formula is often used that depends only on temperature fluctuations: $\langle \Delta E^2 \rangle = k_B C_V T^2$ (see, e.g., [6], where this formula is given with a reference to the well-known textbook [7]). The same formula is proposed in [23] for energy fluctuations in the NVT ensemble. That is, in this case, it is assumed by default that, in simulations, volume fluctuations are zero and can be disregarded. Volume fluctuations in NVT/NVE ensembles are a complex issue, although instantaneous volume values are calculated in the NPT ensemble. We established previously in [9] that, in a two-dimensional Lennard-Jones system near the liquid–crystal transition, the heat capacities obtained from temperature and internal energy fluctuations differ significantly (the former gives underestimated values, while the latter gives overestimated values). However, we neglected volume fluctuations in that case. In the helium system at $T = 298$ K and $P = 0.2$ GPa, the situation is reversed, and the heat capacity obtained from internal energy fluctuations, $C_V = 1.58 k_B$, is lower, even if only slightly, than the 'true' heat capacity (per atom). In this case, in approximately ideal helium, volume fluctuations can be disregarded in calculating thermodynamic quantities due to the approximate equality $(\partial E/\partial V)_T \approx 0$. If we approach energy fluctuations (obtained in simulations in the NVT ensemble) with the formulas from Landau–Lifshitz [1], then, in order to describe energy fluctuations, the fluctuating temperature alone is not enough, and volume fluctuations must also be present. Volume fluctuations can be eliminated from the formulas for energy fluctuations (5) and pressure (2);

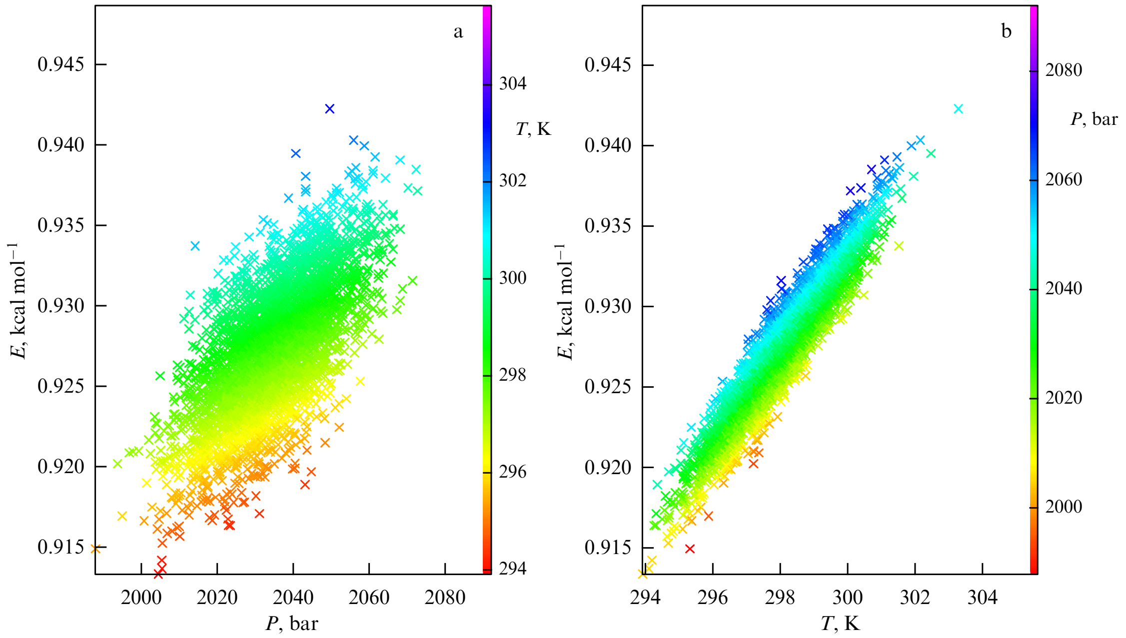

Figure 2. Fluctuations in internal energy E depending on fluctuations in (a) pressure P and (b) temperature T. From graphs, respective linear dependence $E = f(T)$ $(E = f(P))$ at a fixed P (T) is manifested.

the energy fluctuations then depend on pressure and temperature fluctuations. This is exactly what is observed in simulations in the NVT ensemble. For illustration, Fig. 2 shows the fluctuations in energy in helium fluid at one point, from which the linearity of the internal energy in T and P must be obvious. Thus, it follows that, when using the formula for fluctuations in internal energy to calculate heat capacity, it is necessary to take volume fluctuations into account.

At the same time, as can be seen from Fig. 1, fitting the average values of thermodynamic quantities at first glance gives significantly more accurate values of thermodynamic parameters than those that follow from estimates with fluctuations taken into account (in this system, they contribute a relative error $\Delta T/T \approx \Delta P/P \approx 1/\sqrt{N}$). It may seem that this allows invoking the central limit theorem, which states that, for a sample of K values of a random variable with standard deviation σ^2, as K increases, the distribution of the sample mean tends to a normal distribution with the standard deviation σ^2/K. This allows substituting the concepts and taking the variance of the sample mean, which is $\sqrt{K}$ times smaller, as the 'accuracy of measuring' a random variable. In addition to the fact that such an approach, regardless of the amount of noise in the system, allows the 'accuracy' to be made arbitrarily close to zero for a sufficiently large sample, fundamental objections can be raised against it. Indeed, what is so remarkable about the mean value over a sample that it is declared the 'true value' of a random variable?

A possible answer to this question is that this choice is based on an intuitive hypothesis about a symmetric distribution of noise in the system, whereby we can filter out the noise by taking the mean. It is shown in Landau and Lifshitz's textbook that thermodynamic fluctuations are distributed symmetrically (and, moreover, normally), but, from a more general perspective, with sufficiently extensive statistics available, this statement can be subjected to 'experimental verification.' We check the temperature fluctuations in helium under the same conditions (see Fig. 3, which shows the fluctuation distribution density at four pressure values and a nominal temperature of 298 K). The distribution density was calculated using the 'density' function with default parameters from the popular statistical software package R [24]. It is clear that, in all four cases, the mean is close to 298 K, but the probability density function differs significantly from the Gaussian one (in Fig. 3, a Gaussian curve fit is shown for one of the density values). Figure 3 also shows the difference between the simulated data and their fit, which demonstrates not only the 'non-Gaussianity' of the original data but also the presence of a small but noticeable asymmetry in the distribution density. Thus, when moving to increasingly larger samples, we sooner or later encounter a similar asymmetry in the distribution density. All this demonstrates that the application of the central limit theorem demands a high degree of caution (and skepticism).

To illustrate the ambiguity in the concept of the mean value in asymmetric distributions, we give another example concerning an ideal gas and the velocity distribution in it. As is known, the velocity distribution obeys the (asymmetric) Maxwell law. But what asymptotic behavior do the phonon velocity excitation spectra in fluids reach at high temperatures and large wave vectors? The correct answer, obtained by computer simulation in [25], is the most probable (and not the mean) velocity, $v_{\mathrm{p}} = \sqrt{2k_{\mathrm{B}}T/m}$. This once again emphasizes the need for caution in applying the central limit theorem to asymmetric probability distributions. It is also interesting to note that the difference from the normal distribution has been proved rigorously for one-dimensional chains of random resistances [26], which also refutes the widespread opinion about the alleged 'universality' of the Gaussian law.

The conclusions of the theory in Landau's and Lifshitz's textbook concerning the normality of the distribution of temperature fluctuations can be reconciled with the obvious non-Gaussianity of thermal fluctuations observed in simulations by using the concept of algorithmic fluctuations proposed in [9]. Algorithmic fluctuations, by definition, are caused by factors associated with the computer implementa-

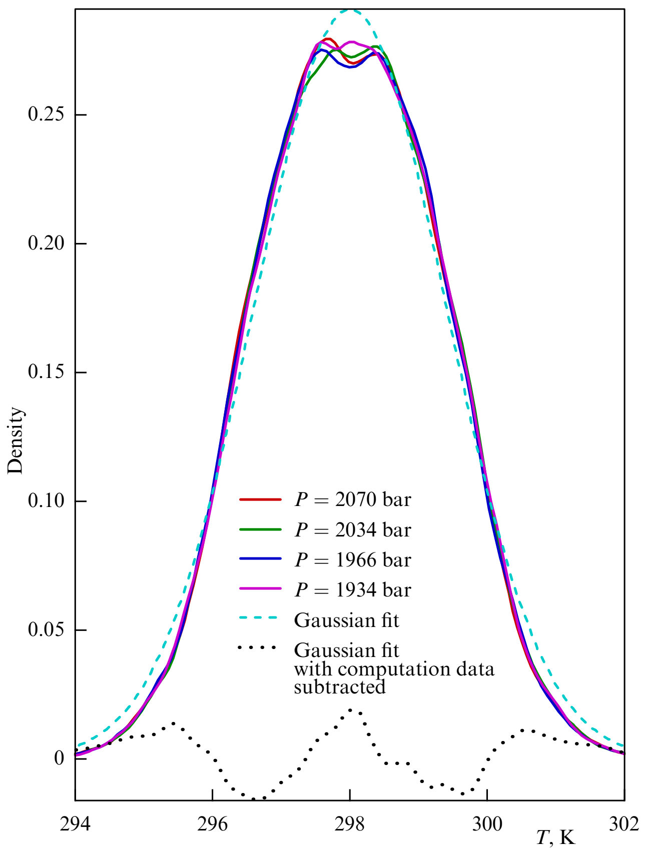

Figure 3. Density distribution of temperature fluctuations in four isothermal simulations at $T = 298$ K and different pressures (solid curves). Dashed line: fitting to normal distribution of curve obtained at $P = 1934$ atm. Dotted line: difference between values obtained in simulation and their fitting to normal distribution.

tion of the computation algorithm: the discreteness of time, the limited computation time, and so on. Similar ideas were previously expressed in [18], where the concept of K-entropy was used to describe the effects associated with these limitations. At the same time, our computations show that a decrease in the integration step over time leads to a qualitative change in the distribution function of thermal fluctuations. Thus, for an integration step of 0.1 and 0.5 fs, the distribution becomes closer to the normal one than the distribution in Fig. 3 is, although the standard deviation of the fluctuations remains almost unchanged. This indicates that the algorithmic temperature fluctuations (which are expected to increase with the integration step) have a non-Gaussian distribution function in our system, and therefore the concept of entropy is apparently inapplicable to them. At the same time, to correctly isolate the contribution of algorithmic fluctuations, a comparative analysis of fluctuations as functions of the integration step is required, which (as our experience suggests) may be a very time-consuming procedure. The good news is that the fluctuation distribution function is independent of the total integration time, and therefore the general idea of the distribution function can be obtained by integrating over fairly short distances.

4. Conclusions

We have examined two approaches to studying thermodynamic fluctuations in computer simulations: one is based on the theory presented in Landau's and Lifshitz's textbook [1], assuming a self-consistent solution to the problem and the second is developed in the work of Lebowitz–Percus–Verlet et al. [10, 11], in application to a limited class of computer simulation problems using the classical molecular dynamics method. Studies of fluctuations in molecular dynamics simulation of helium fluid at room temperature and a pressure of 2 kbar have shown that they differ by several times depending on the type of ensemble (NVE or NVT) used in the computation. For the NVT ensemble, the best result is given by the Landau–Lifshitz approach, and for the microcanonical NVE ensemble, by the Lebowitz–Percus–Verlet approach. At the same time, a difference from the normal distribution was established for the distribution function of temperature fluctuations in this system in the NVT ensemble. It was shown that such a difference is associated with the presence of so-called algorithmic fluctuations caused by the computer implementation of the calculation algorithm: the discreteness of time, a limited computation time, and so on. The fundamental possibility of reconciling the weakly conservative laws of particle motion (with the energy conserved on average) with the obvious asymmetry of the time evolution of the system as a whole was demonstrated.

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