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Original article

Inherent noise present in molecular dynamics simulations and what can be learnt from it for 2D Lennard–Jones system

Mikhail V. Kondrin[1,a], Yulia B. Lebed[2,b]

[1]Institute for High Pressure Physics RAS, 108840 Troitsk, Moscow, Russia,
[2]Institute for Nuclear Research RAS, 117312 Moscow, Russia

[a]mkondrin@hppi.troitsk.ru, [b]jlebed@inr.ru

Corresponding author: Mikhail V. Kondrin, mkondrin@hppi.troitsk.ru

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ABSTRACT We have investigated the influence of finite number of particles used in molecular dynamics simulations on the fluctuations of thermodynamic properties. As a case study, the two-dimensional Lennard–Jones system was used. The 2D Lennard–Jones is an archetypal system and a subject of long debate about whether it has continuous (infinite-order) or discontinuous (the first-order) melting transition. We have found, that anomalies on the equation of state (the van-der-Waals or Myer–Wood loops), previously considered a hallmark of the first order phase transition, are at best at the level of noise, since their magnitude is the same as the amplitude of pressure fluctuations. So, they could be regarded as a statistically unsignificant effect. Also, we estimated inherent statistical noise present in computer simulations, and came to the conclusion, that it is larger than predicted by statistical physics, and the difference between them (called algorithmic fluctuations) may be due to the computer-related issues.

KEYWORDS 2D/3D Lennard–Jones system, melting, fluctuations, bulk modulus, specific heat

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1. Introduction

Brownian motion of small particles in a finite size system inevitably leads to fluctuations of thermodynamic parameters. In thermodynamic limit (infinite system size), fluctuations decrease, so we can safely deal with average parameters.

However, molecular dynamics and, in general, any computer simulations, use quite small finite size systems. This rises a question of how close we are to the thermodynamic limit. To answer this question, we have to estimate the system's fluctuations.

This problem was previously acknowledged in the paper of Hickman and Mishin [1], but they considered only the fluctuations of temperature. Their work outlines fundamental problem with temperature fluctuations in computer simulations, the explanation of which can be found in a well-known course of theoretical physics [2], giving a result, that relative fluctuations of thermodynamic parameter are roughly inversely proportional to the square root of the number of particles in the system.

If we limit ourselves to description of NVE ensemble (with constant number of particles N, volume V and energy E), pressure and temperature of the system are expected to fluctuate around some average values. Classical statistical mechanics predicts [2] that fluctuations of pressure P and temperature T of large enough system are distributed according to the Gauss law with standard deviations:

$$\Delta T^2 = \frac{k_B T^2}{N c_V}, \tag{1}$$

$$\Delta P^2 = -k_B T \left(\frac{\partial P}{\partial V}\right)_S = \frac{k_B T}{V} B_S. \tag{2}$$

Here, k_B is the Boltzmann constant, c_V is the specific heat at constant volume per particle, B_S is the adiabatic bulk modulus, index S stands for constant entropy. The second formula in the case of ideal gas gives:

$$\left(\frac{\Delta P}{P}\right)^2 = \frac{\gamma}{N},$$

where γ is an adiabatic exponent. This implies the general law that relative fluctuations of thermodynamic parameters scale approximately to the square root of the system size. This conclusion is corroborated by computer simulations of fluctuations of pressure in non-ideal plasma [3]. So, for typical system size used in molecular dynamics simulations

($N \leq 10^5$), relative fluctuations are slightly less than 1 %. While for *ab-initio* molecular dynamic simulations, the situation gets worse, since the number of atoms doesn't exceed several hundreds, and fluctuations can reach 10 %.

To test these assumptions, we have chosen the two dimensional Lennard–Jones (2DLJ) system [4]. It is an archetypical model in computer simulations, and much attention was paid to determining the type of its melting transition. Original theory of 2D crystal melting dates back to the 70s (the Berezinskii–Kosterlitz–Thouless–Halperin–Nelson–Young theory) and suggests, that melting is an infinite-order, two-stage transition between crystal and liquid. The first stage – crystal to hexatic phase transition, occurs with the loss of translational order, and the second stage – hexatic to liquid – with the loss of orientation order, see e.g. [5]. For this theory Kosterlitz and Thouless in 2016 were awarded the Nobel prize. For simplicity, we will call it continuous model. However, almost immediately this model was contested with computer simulation study [6], suggesting the first order of phase transition in the 2DLJ system. Subsequently, the number of works addressed to this system [7–15] and gave controversial opinions on the character of melting transition. Hot debates followed through 1980 – 1990s, but did not lead to a clear conclusion, the echo of these debates continues until recently [16–21]. It is worth mentioning, that first order transition was predicted by the authors, who used rather a small system of $N < 10^4$ particles, continuous transition was claimed based on a larger system up to $N = 10^5$, and intermediate position – for the system with $N = 2500$ particles [17]. The most recent paper with $N = 512^2$ particles [21] favored the first-order transition. It seems, that the authors' opinions are unconsciously effected by the scale of fluctuations. The most important are pressure fluctuations which influence the shape of equation of the state (P–V) curve. Usually, the presence of van-der-Waals loops on the P–V curve (or the Mayer–Wood loop on $P - \rho$ where ρ is numerical density) is considered a decisive indicator of the first order transition. Still, in many of these works, the depth of the loops is rather shallow, and does not allow to choose the first- or continuous order of phase transition. The most convincing would be to compare the effect observed with inherent system noise due to thermal fluctuations.

The specific objective of the paper is an investigation of the crystallization in 2D Lennard–Jones system and comparison of the amplitude of van-der-Waals loop reported to be observed there with the intrinsic fluctuations present in the system. It will be demonstrated that in currently available research van-der-Waals loop is at best 1-σ effect so it is surely not enough to overthrow existing Nobel prize winning theory. Also it will be demonstrated that observed fluctuations are mainly connected to thermodynamic fluctuations predicted by statistical physics.

2. Methods

We have tested validity of theoretical predictions by computations with classical molecular dynamics simulations of the 2DLJ system as implemented in state of art LAMMPS software package [22, 23]. Input files from Carsten Svaneborg group home page [24] were adapted to our needs. We used NVE ensemble with Langevin thermal dynamics with time step 0.01 LJ units. We used $5 \cdot 10^4$ steps for thermal equilibration and next $5 \cdot 10^4$ steps for estimation of thermodynamic parameters and their fluctuations. Validity of this choice will be explained later. As a rule, we used $N = 10^4$ particles. Some of the results were checked with larger system containing $N = 10^5$ particles. Also, longer simulation times and NVT ensemble were used. Changing the ensemble to NVT with Nose-Hoover thermostat slightly influenced the result making the system fluctuate around initially set temperature, but the amplitude of fluctuations did not change. Starting configuration of particles was chosen randomly with initial minimization of energy to avoid overlapping of the particles. Random configuration taken by us illustrates crystallization of liquid, rather than crystal melting. The order of crystal-liquid phase transition should not be influenced by the direction of the phase transition. The temperature was varied in the range $T = 0.6 - 1.1$ with step 0.1 and density range $\rho = 0.55 - 1.25$. To compare our findings with previous results, the temperature $T = 3.0$ near the melting transition was investigated. Distribution density of thermal fluctuations was estimated by *density* function with default parameters as implemented in R software package [25].

3. Results

Fluctuations of pressure and temperature of system with $N = 10^4$ particles at $T = 0.9$ are shown in Fig. 1 at the same set temperature $T \approx 0.9$ and different densities ($\rho = 1.23$ and $\rho = 0.86$) which correspond to thermodynamic conditions deep inside the crystal phase and the liquid phase just below the transition. As it was expected, fluctuations of temperature reach about 1 % with almost normal distribution (see Fig. 2). The P-ρ curves in vicinity of these density-temperature conditions (near the melting transition) are shown in Fig. 3. It is clear, that no van-der-Waals loops are observed in this region and with precision of pressure fluctuations they might be considered as monotonous functions increasing with the density rise. Still we need to inspect fluctuations of temperature to make decisive conclusions.

As it is clear from distribution functions of temperature along nominal isotherm $T = 0.9$ (see Fig. 2) there is distinctive shift of temperatures to higher values of temperature than the one initially set at densities corresponding to solid state of the 2DLJ system. When approaching the melting transition this curve at $\rho \approx 1$ exhibits a clear crossover to lower temperatures and at these densities distribution curve is clearly bimodal. Presumably this is due to the ensemble (NVE) chosen by us where the energy of the system is kept constant but not the temperature, and slow pressure relaxation in the crystal phase (see Fig. 1) leads to deviation of temperature from the set value. Therefore temperature can not relax fast enough to follow temperature of the heat bath governed by Langevin dynamics. Still, we should stress that near

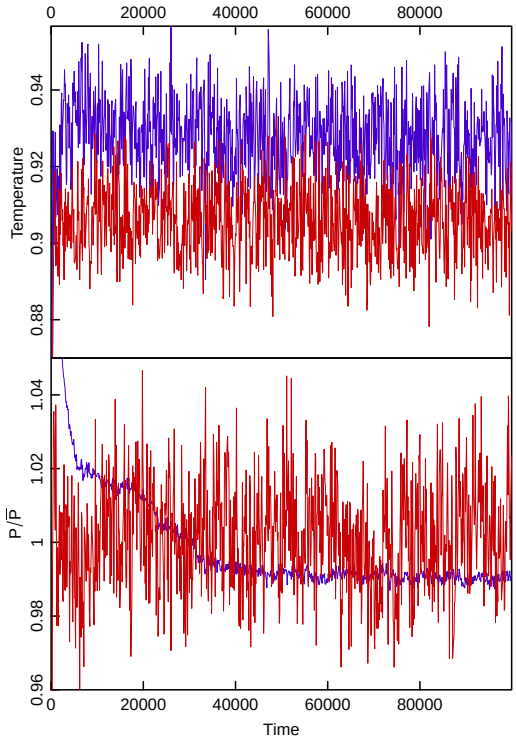

FIG. 1. Fluctuations of temperature (upper panel) and relative pressure (lower panel) at $T = 0.9$ and two different densities $\rho = 1.23$ (blue curves) and $\rho = 0.86$ (red curves) which correspond to the states deep inside the crystal phase and in the liquid phase just below the transition respectively.

the melting transition the mean value of the temperature distribution function is constant and only slightly shifts above initially set value which is independent of density values.

For comparison we provide distribution densities obtained for the same number of particles in the same conditions, but for NVT ensemble (Fig. 4). As expected, for this kind of ensemble the distribution maximum (mean value) is closer to the initially set temperature value. However, the standard deviation is almost the same as in NVE ensemble. It is interesting to note that at $\rho \approx 1$ the distribution is also bimodal. This fact possibly catches an important feature in the dynamic of the system presumably arising from transition from the crystal to hexatic phase.

To demonstrate this idea, we provide the results for a larger NVE ensemble with $N = 10^5$ particles at the same temperature $T = 0.9$ in the nearest vicinity of the transition (see Fig. 5). As expected, with the rise of the particles number, the values of fluctuations of temperature and pressure decrease, but slow relaxation of pressure is conserved on the crystal side of transition. However, at the upper half of time frame used for calculation of thermodynamic parameters, the relaxation almost reaches its equilibrium value which is demonstrated by the density distribution of temperature fluctuations in this time region (see Fig. 6). It is clear that the mean temperature is only slightly above the initially set one and the drift of the mean temperature is negligible in comparison to the standard deviation of fluctuations. This means that the absence of the van-der-Waals loops on the pressure-density curve observed in Fig. 5 is not related to the drift of temperature at higher densities.

To compare our findings with the previous results [21], we performed calculation at higher temperature $T = 3.0$ in NVE ensemble and $N = 10^5$ particles (see Fig. 7). In the work of Tsiok *et al.* [21], calculations were done in NVT ensemble at the same $T = 3.0$ temperature, but with larger number of particles $N = 256^2$. It was stated there, that the van-der-Waals loops were observed, which showed the first-order of the transition at least at hexatic-liquid stage. Still, the van-der-Waals loop observed there had rather small amplitude (in Fig. 7 it looks like a plateau), being significantly smaller than standard deviations of pressure fluctuations calculated by us.

By the way, fluctuations observed in the middle of transition, shown in the inset of Fig. 7 demonstrate convergence of pressure relaxation at longer time range ($t = 2 \cdot 10^5$). From this demonstration it is evident that the time range used by us (upper half of $t = 10^5$ interval) is large enough to fully converge the pressure values in the vicinity of melting transition.

There is qualitative difference between the two curves in Fig. 7 – plateau on the curve of Tsiok *et al.* [21] is not only more flat than the one reported by us, but also spans a longer range of densities ρ. To explain this discrepancy, we can refer to the difference between initial conditions in our work and Ref. [21]. In our setup, initial atom coordinates were

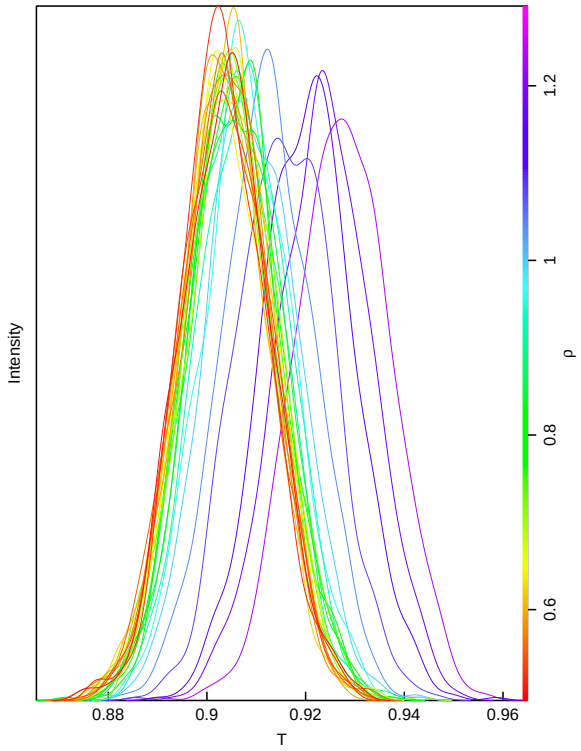

FIG. 2. Distribution density of thermal fluctuations at $T = 0.9$ and different densities with $N = 10^4$ particles calculated in NVE ensemble. Density values are encoded in the color key at the right side of the plot

purely random but in Ref. [21], they started from ideal triangular lattice. The latter case favors stability of crystal phase, so it persists longer below melting transitions which results in the van-der-Waals loops on equation of state curve. Flatness of this curve depends on the number of system's particles, so at the thermodynamic limit (infinite particles number) the van-der-Waals loop is believed to transform into ideal plateau with zero derivative in the middle. It was demonstrated for the first time for the 2DLJ system [8] that deepness of the van-der-Waals loop in the system with "crystalline" initial state is correlated with the number of particles – the larger the number, the more shallow the curve. From this work one can see that the amplitude of van-der-Waals loop has the same order of magnitude as system fluctuations. In Ref. [8] for $N = 256$ system both values are about 10 %, which corresponds to the rule of thumb, that relative fluctuations are inversely proportional to square root of the number of particles.

There is another argument in favor of the first-order phase transition, namely, phase coexistence observed in computer experiments between hexatic and liquid phase in the region of "van-der-Waals loop" [21]. We did not investigate this problem closely, but previous report obtained by Patashinskii *et al.* [17] in $N = 2500$ 2DLJ system demonstrates that this separation has transient character, so that regions of hexatic phase and translational disordered liquid freely transform into each other. In our opinion (we agree with authors of Ref. [17]), such a transformation is an indication of continuous transition between the two phases.

There were two recent papers proposing different scenarios of the first order phase transition [19, 20]. Rather than discussing contradictions in various simulations, we would like to draw attention to the point – how many sigmas are there in the deepness of the van-der-Waals loops? In other words, we insist on the importance of being earnest with the error bars. Comparison with the noise band of pressure relaxation curve reported in our paper demonstrates that it is also much below 1-sigma. The recent paper [26] where the fluctuations were averaged over 5 replicas at $T = 3.0$ demonstrated that the error bars are comparable with amplitude of van-der-Waals loop so effect is about 1-σ. So, there is no point to discuss such a negligible effect. The effect should be no less than 3-sigma, to be statistically significant. Our estimate is that to rise statistical significance upto at least 3σ averaging should be done over 45 replicas. However, effect and noise in 2DLJ system are correlated – the larger the system size, the smaller the noise, and the shallower van der Waals loops [8, 26]. In fact, this is discussed in [19] as size effect– energetic barrier between hexatic phase and liquid diminishes as $1/\sqrt{N}$ with the system size. Hence, in the thermodynamic limit, this means that energetic barrier between two phases vanishes,

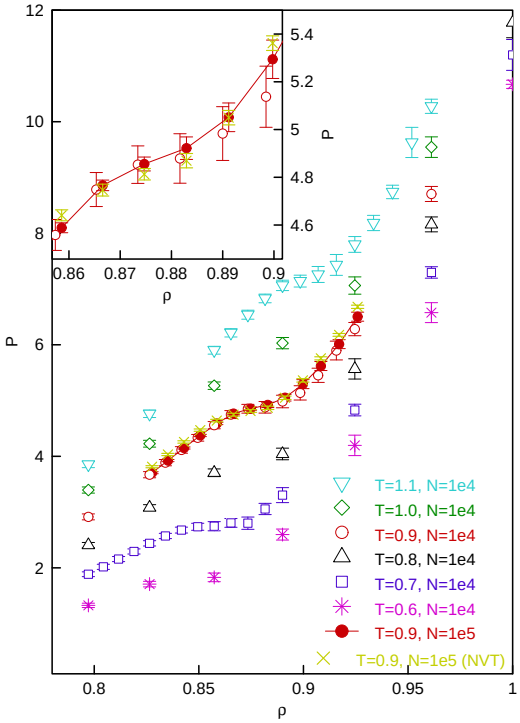

FIG. 3. Equation of state at different temperatures in the vicinity of melting transition. The inset shows enlarged region in the vicinity of transition at $T = 0.9$ calculated for different ensembles and numbers of particles N (see list in the main panel). The type of ensemble if not indicated in the plot means NVE ensemble.

that is transition is continuous, therefore it should be in full agreement with conclusions of the Berezinskii–Kosterlitz–Thouless–Halperin–Nelson–Young theory. Therefore, there is not enough evidence of a first order type of hexatic-liquid transition to overthrow existing theory of 2D melting.

There is also one more fundamental problem of claiming the first-order melting in 2D systems. The first-order phase transition (and other finite order transitions) in 2D melting contradicts the Mermin–Wagner theorem, which states that spontaneous continuous symmetry breaking is impossible at finite temperatures at dimensions $d \leq 2$. Continuous symmetries in liquids are isotropy and translational invariance. Existing theory of 2D melting (the theory of Berezinskii–Kosterlitz–Thouless–Halperin–Nelson–Young, was specifically designed on the basis of the Mermin–Wagner theorem, as it was literally quoted by V. L. Berezinskii in the beginning of his seminal paper [27]) in elegant way avoids this theorem by demonstrating that the melting transition in 2D is not spontaneous but continuous (an infinite order one). In other words, solid and liquid states differ only in quantitative, not qualitative degree of disorder. However, the Mermin–Wagner theorem deals with thermodynamic limit, that is, with infinite system. Still, in a finite system, it is possible for statistically insignificant effects, resembling the first-order melting transition to take place. However, they should be regarded as manifestation of a system finiteness ("size-effects") and should tend to zero as the system size increases. Therefore, they should disappear in the thermodynamic limit. Exactly this is demonstrated by investigation of melting in 2DLJ system [19, 20] but not the first-order melting in 2D as the authors of the cited works claimed.

Later we will demonstrate that the noise observed in the 2DLJ system mostly matches the predictions of statistical physics.

4. Discussion

Previously, we have demonstrated the finite precision of molecular dynamic simulations. In this section, we answer the second part of the question posed in the title – what can we learn from finite precision of molecular dynamics experiments. As follows from Eqs. (1)–(2), we could estimate isochoric heat capacity and adiabatic bulk modulus from fluctuations of temperature and pressure.

According to Eq. 1, we can obtain c_V from standard deviation of relative fluctuation of temperature. This plot *vs.* density ρ for temperatures in the range $T = 0.6 - 1.1$ is depicted in Fig. 8. Overall plot is rather fuzzy, but for a fixed temperature (see dashed line in Fig. 8 which is a free-hand draw for $T = 0.9$) we can conclude that the heat capacity

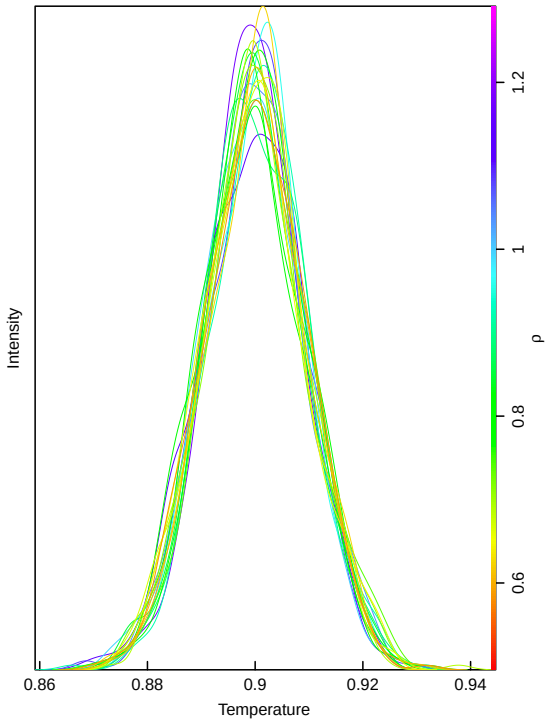

FIG. 4. Distribution density of thermal fluctuations at $T = 0.9$ and different densities with $N = 10^4$ particles calculated in NVT ensemble. Density values encoded in the color key at the right side of the plot

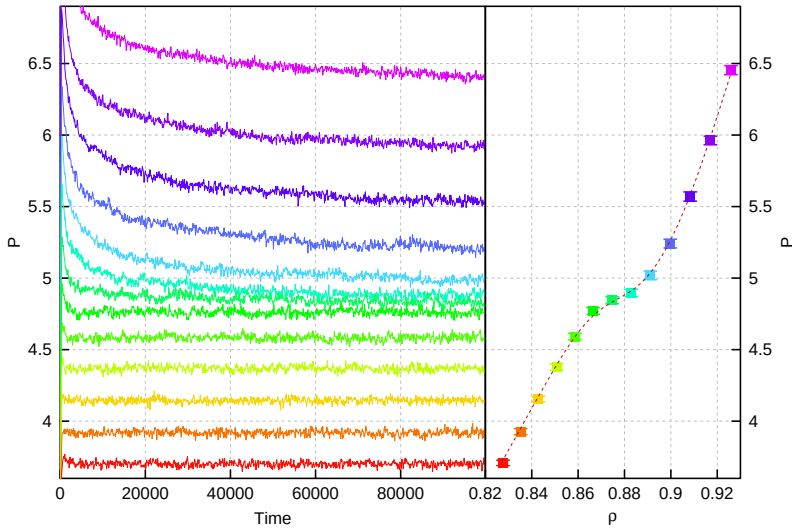

FIG. 5. Fluctuations of pressure in the vicinity of melting transition at $T = 0.9$ (left panel) and corresponding equation of state (right panel) for larger ensemble with $N = 10^5$ particles.

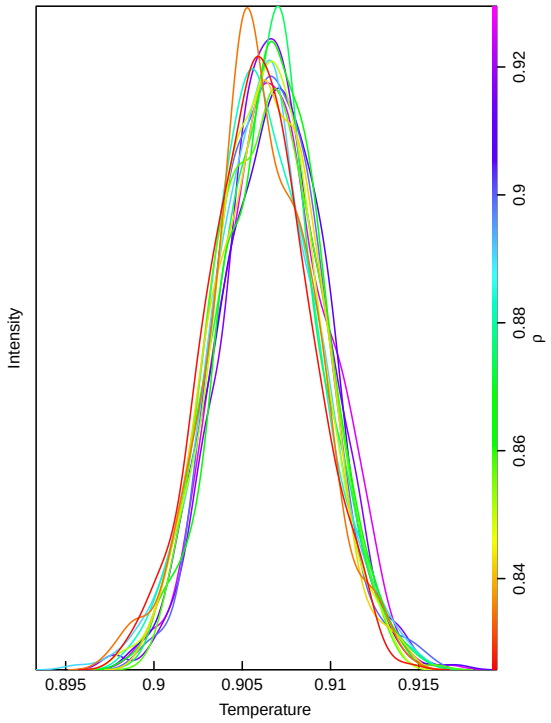

FIG. 6. Distribution density of thermal fluctuations in the vicinity of melting transition at $T = 0.9$ and different densities for larger ensemble with $N = 10^5$ particles. The values of density are encoded in the color key at the right side of the plot.

is almost constant at the whole densities range. It is interesting to check the validity of the $N^{-1/2}$ scaling law for fluctuations. We plotted the data obtained for $N = 10^5$ ensemble on the same Fig. 8. It is clear that in comparison with $N = 10^4$ ensemble data, there is small but regular discrepancy between them in the range of about 15%. It means that fluctuations in computer simulations are larger, than those predicted by statistical physics. These fluctuations could be due to other inputs, unrelated to statistical physics, for example, finite precision of computer calculations, discretization of time in molecular dynamics simulations, incomplete structure relaxation because of finite time of computer experiments, Gaussian random force in computer realization of Langevin thermostat *etc*. We don't want to call these fluctuations "unphysical" so we will name it algorithmical in contrast to physical ones described by Eqs. (1)–(2). It is hard to estimate the scaling of algorithmical fluctuations with the system size, but the difference between the amplitudes of fluctuations observed in $N = 10^5$ ensemble and for $N = 10^4$ one (see Fig. 8) suggests that their contribution relative to physical fluctuations will rise with the increase of system size. May be it is not due to the absolute increase of algorithmical fluctuations but rather to decrease of physical ones. At least our recent work [28] demonstrated that in 3D Lennard–Jones system in NVT ensemble with Nose-Hoover thermostat integrated at much finer time step these algorithmical fluctuations are negligible. We should also mention that almost constant c_V value during transition was obtained in seminal work of Frenkel and McTague [7] although with higher value of $c_V = 2$. This discrepancy deserves special attention.

Eq. (1) is not new in molecular dynamics simulations but it is known in different flavor as fluctuations of internal energy U (per particle):

$$\Delta U^2 = \frac{k_B T^2 c_V}{N}, \tag{3}$$

which is a consequence of Eq. (1) and thermodynamic identity $\Delta U = c_V \Delta T$. For example, this formula Eq. (3) was used for calculation of specific heat in the system of the Hertzian disks in Ref. [29] (the authors referenced the readers to the book [30]). Generally speaking, Eqs. (1)–(3) can be regarded as thermodynamic counterpart of famous fluctuation-dissipation theorem [2, 31, 32] where fluctuations are related to the value of certain material characteristic, such as heat capacity and adiabatic bulk modulus. However, applicability of these equations to the results obtained in computer simulations is problematic. Because of the presence of algorithmical fluctuations c_V values obtained from the temperature and internal energy fluctuations (Eq. (1) and Eq. (3) respectively) will be different. Obviously Eq. (1) will underestimate real c_V and Eq. (3) will overestimate it. Similarly Eq. (2) should overestimate the real adiabatic bulk modulus. Considering relative input from physical and algorithmical fluctuations to the overall noise, we should arrive at quite paradoxical

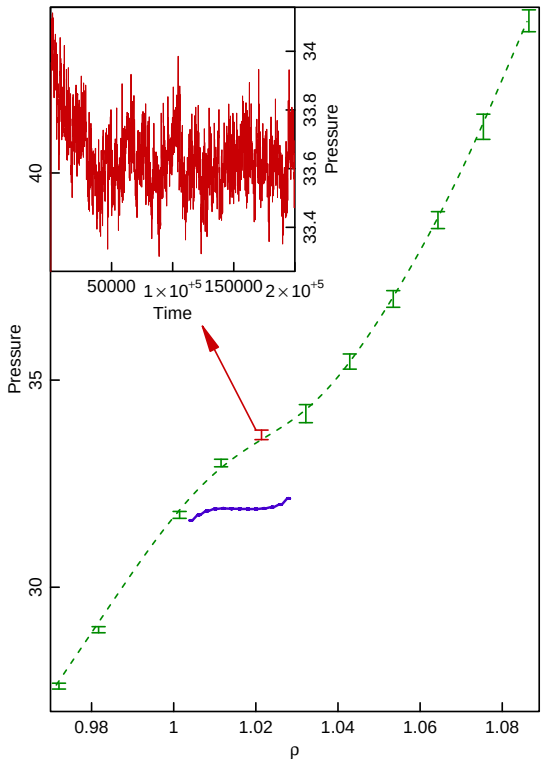

FIG. 7. Equation of state in the vicinity of melting temperature calculated in this work for NVE ensemble with $N = 10^5$ particles at $T = 3.0$ (green dashed curve is guide to the eyes). Blue curve is the data for NVT ensemble for $N = 256^2$ particles at the same temperature obtained in Ref. [21]. Inset shows temperature fluctuations for the chosen (marked in red) point in the middle of the melting transition.

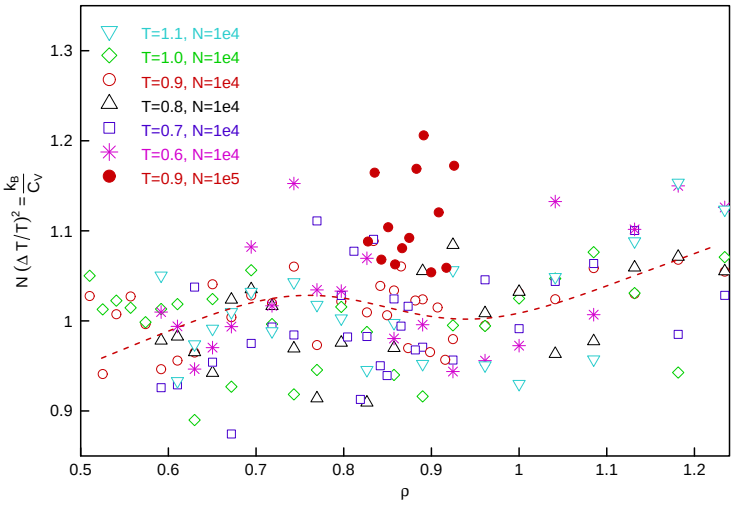

FIG. 8. Heat capacity of the 2DLJ system estimated from thermal fluctuations by Eq. (1). Dashed curve is guide to the eyes for c_V values corresponding to $T = 0.9$.

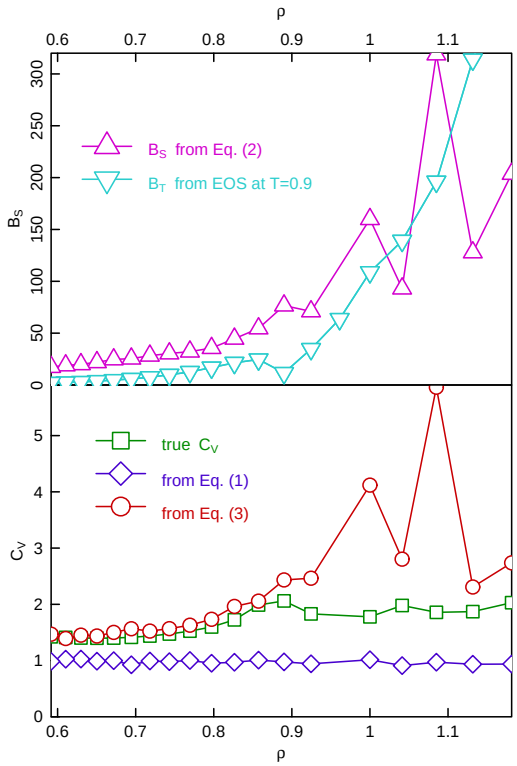

FIG. 9. Adiabatic bulk modulus B_S and heat capacity c_V evaluated from Eqs. (1)–(3). "True" c_V and isothermal bulk modulus B_T are evaluated by numerical differentiation of internal energy along isochores and equation of state $P(\rho)$ along isotherm $T = 0.9$ respectively.

conclusion that estimates of thermodynamic parameters from fluctuations in computer simulations will be more precise being obtained from smaller systems, where larger physical fluctuations dominate over algorithmical ones.

Regarding Eq. (3), one should be cautious because it contains only one part of internal energy fluctuations depending on temperature fluctuations. More general equation (which can be look up in Ref. [2]) depends also on volume fluctuations. However in molecular dynamics simulations in NVE and NVT ensembles, volume V is kept constant by definition and it is taken equal to the volume of simulation cell. So this term can be safely ignored in computer calculations.

The results of estimation of specific heat and adiabatic bulk modulus from fluctuations according to Eqs. (1)–(3) for $N = 10^4$ system are depicted in Fig. 9. For calculation of "true" specific heat we used the values of internal energy along isochores in the temperature range $T = 0.6 - 1.1$ and numerically differentiated it by temperature. In most cases the curves require linear fit of U *vs.* T because the dependencies hardly deviate from linear ones. To check the validity of adiabatic bulk modulus estimation we used isothermal bulk modulus B_T obtained from numerical differentiation (simple ratio of finite differences) of equation of state $P(\rho)$ taken at $T = 0.9$. B_T is related to adiabatic bulk modulus (which can in practice be measured by longitudinal sound velocity measurements) by equation:

$$\frac{B_S}{B_T} = 1 + \alpha_T \chi T.$$

In solids the thermal expansion coefficient α_T is small and the Grüneisen parameter χ is close to unity, so deviation of this ratio from unity is negligible. At the same time, this difference in liquids can amount to 20 % (due to larger α_T) [33]. Note that the adiabatic bulk modulus is always greater than isothermal. Adiabatic bulk modulus is discontinuous in the process of the first-order phase transition [34].

As it follows from Fig. 9, the "true" c_V is nicely bracketed by estimations from thermal fluctuations. At the same time, "true" c_V does not show any discontinuity at the region of phase transition but gradually diminishes from the values $c_V \approx 2$ in the solid phase (the Dulong–Petit law in 2D) to about 1.5 in the liquid phase. These calculations corroborate continuous character of the phase transition. From the values of "true" c_V, we can estimate contribution of algorithmic fluctuations to the temperature fluctuations of $N = 10^4$ ensemble. It is easy to observe that in this case algorithmic fluctuations contribute to almost 50 % of $(\Delta T/T)^2$ in the solid phase and ≈ 30 % in the liquid phase.

There is quite different approach to temperature fluctuations which produces different estimates in comparison to statistical physics one predicted by Eq. (1). It was specifically designed to describe temperature fluctuations in classical

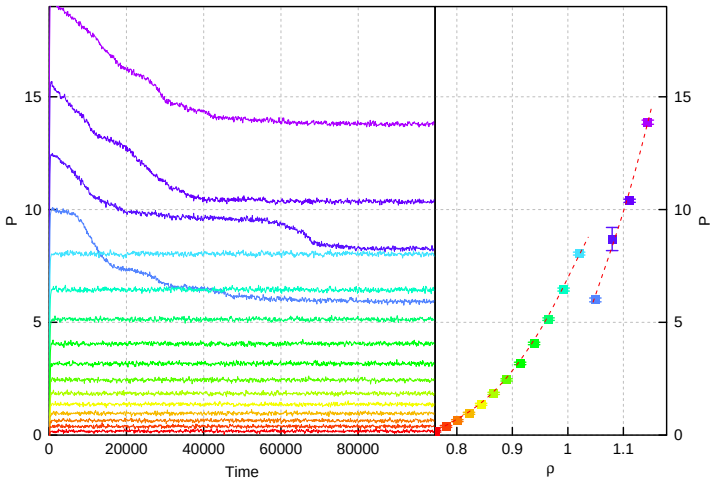

FIG. 10. The pressure relaxation curves (left panel) and equation of state at $T = 0.9$ (right panel) in three dimensional Lennard–Jones system. Dashed red curves at the right panel are guides to the eyes.

molecular dynamics simulations in NVE ensemble and for 2D case it states [35, 36]:

$$\Delta T^2 = \frac{T^2}{N}\left(1 - \frac{k_B}{c_V}\right). \tag{4}$$

This equation can be derived from Eq. (14) in Ref. [36] for fluctuations of kinetic energy with obvious modification from 3D to 2D case. Still, it can be demonstrated that this formula predicts lower values of temperature fluctuations than the one shown in Fig. 8. For $N = 10^4$ ensemble (if all fluctuations are supposed to be described by this formula Eq. (4)) this yields the value of $c_V \approx \infty$ and produces no reasonable value for $N = 10^5$ ensemble. Therefore in this case we also arrive to conclusion that at least partially observed temperature fluctuations contain algorithmic noise. In case of $N = 10^4$ ensemble the contribution of algorithmic noise to $(\Delta T/T)^2$ can be estimated as 50 % in the solid phase and as 70 % in the fluid phase. So, contribution of algorithmic fluctuations in the same $N = 10^4$ ensemble is even greater than predicted by Eq. (1).

The case of B_S is slightly more complicated. As expected B_S is larger than B_T in liquid and hexatic phases, but deep inside the crystal phase there are points where estimated adiabatic bulk modulus is smaller than isothermal one (although we expected that B_S should be overestimated). The only reasonable explanation for this anomaly is that there are slow physical fluctuations in the solid phase, which require longer time for their registration than our time frame. Taking into account the presence of slow pressure relaxations in solid state (see Fig. 5) it is naturally to assume that slow fluctuations are also possible. To estimate the amplitude of total fluctuations we do not need to relax the system for longer times, the simple estimate would be obtained from the multiplication of the error bars of $P(\rho)$ curve in the solid phase by $\sqrt{\max(B_T/B_S)} \approx 1.8$ times. Surely this operation does not increase statistical significance of van-der-Waals loops reported in the literature earlier. However, we acknowledge that demonstration of slow fluctuations in the solid state requires careful investigation of spectral decomposition of fluctuations, that we are not ready to perform.

5. Comparison with 3D case

The main purpose of this section is brief demonstration of validity of methods used for investigation of 2D Lennard–Jones system in comparison to 3D case. There is no doubt that 3D melting is the first-order transition. So, how would true first-order transition look like in computer simulations? In 3D case we used the same parameters as for calculations of 2DLJ system except for 3 dimensions. We restricted ourselves to NVE ensemble with $N = 10^4$ particles. It allows us to check the convergence of finite time calculations to the final state of transition. As in the 2D case, we start from random initial configuration that is, simulating crystallization rather than melting. It would be demonstrated that possible crystallization into polycrystalline state does not influence much the character of transition. Also by this calculation we would dispel a popular belief, that fluctuations in 3D case are significantly smaller than in 2D case. In both cases fluctuations are governed by the same Eqs. (1)–(3) although with different parameters c_V and B_S.

Equation of state at $T = 0.9$ and pressure relaxation curves at different densities ρ are depicted in Fig. 10. The first conspicuous feature is the amplitude of van-der-Waals loop observed on the equation of state – it is many times larger than the error bars, so the effect is statistically significant. The first order of transition also manifests itself in visual difference of pressure relaxation curves in Fig. 10 and that in 2D case (Fig. 5). It is clear that qualitative difference of pressure

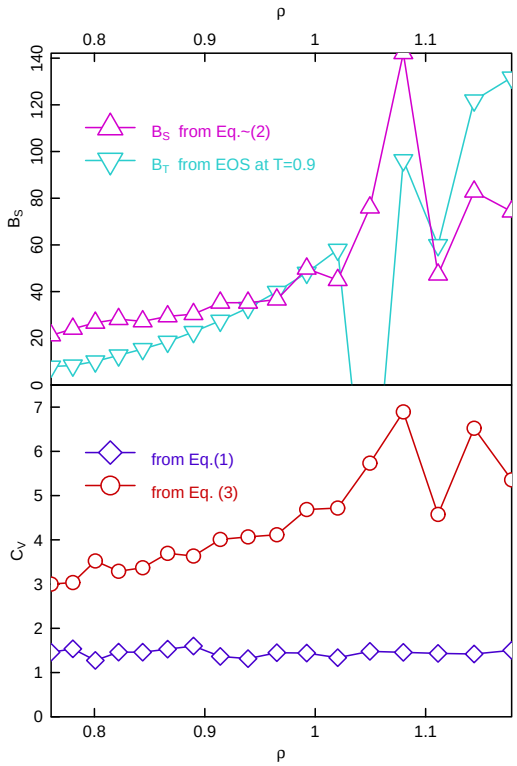

FIG. 11. Adiabatic bulk modulus B_S and heat capacity c_V evaluated from Eqs. (1)–(3) in 3D case. Isothermal bulk modulus B_T are evaluated by numerical differentiation of equation of state $P(\rho)$ along isotherm $T = 0.9$.

relaxation curves in solid and liquid case in 3D – the slow pressure relaxations present in solid state are totally absent in liquid state, and gradually diminishing of slow relaxations during hexatic-liquid transition in 2D case.

Calculations of B_S, c_V from fluctuations and B_T from equation of state are depicted in Fig. 11. The discrepancy between B_S and B_T on the one hand and c_V values obtained from Eq. 1 and Eq. 3 respectively are similar to that observed in 2D case (Fig. 9) although the final values differ.

6. Conclusions

To conclude, we demonstrate that the van-der-Waals loops observed on equation of state of 2DLJ system which were previously considered an indication of the first order phase transition between 2D crystal and liquid are at the level of noise and can't be reliably used to determine the character of transition. This statistically insignificant effect is surely not enough to overthrow the existing Nobel prize-winning theories of 2D melting. The increase of the particles' number used in molecular dynamics simulation can lead to attenuation of standard deviation of fluctuations, but at the same time (as demonstrated before [8]), it results in flattening of the van-der-Waals loops on the equation of state curves. Estimation of inherent statistical noise presented in computer simulations led us to conclusion that it is larger than predicted by statistical physics, and the difference between them (named algorithmical fluctuations) is probably due to computer-related issues.

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Information about the authors:

Mikhail V. Kondrin – Institute for High Pressure Physics RAS, 108840 Troitsk, Moscow, Russia;
ORCID 0000-0001-5978-4530; mkondrin@hppi.troitsk.ru

Yulia B. Lebed – Institute for Nuclear Research RAS, 117312 Moscow, Russia; jlebed@inr.ru

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