Hexatic phase in two-dimensional Yukawa systems: Existence and properties

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Abstract. In present work, phase transitions in strongly-coupled two-dimensional dissipative Yukawa systems are studied. The thermodynamic characteristics of these systems are calculated, namely the internal energy, the specific heat and the entropy. The considered characteristics have two singular points; one of these points corresponds to the first-order phase transition from crystal to the hexatic phase, and another point corresponds to the second-order phase transition from the hexatic phase to the isotropic liquid. The dependence of the position of the melting lines and the range of existence of the hexatic phase on the concentration of the grains in the considered system is studied. The special attention is paid to the comparison of our results to the existing numerical and analytical data.

1. Introduction

One of the most important questions of the modern science is to specify the phase boundaries of a certain matter and the thermophysical properties in each phase [1–4]. As for the mechanism of phase transitions in two-dimensional systems—it is a puzzle that excites the scientists for almost forty years so far. At present, there are several theories describing this process. Hereafter we mention the most distinguished ones.

The Kosterlitz–Thouless–Halperin–Nelson–Young (KTHNY) theory claims that the melting of a two-dimensional crystal begins with the formation of topological defects (dislocations and disclinations), and such a system has two phases with the same packing symmetry [1,5]. In first of them, the positional order, as well as the orientational one, has long range. In the second (so-called hexatic) phase the positional order has short range, but the orientational order is preserved and vanishes only for higher temperatures. Therefore, the system goes from the solid to the liquid state via the formation of the intermediate hexatic phase.

Unfortunately, the KTHNY theory was not clearly proved by numerical experiments. Three years later another theory was born, stating the possibility of the phase transition induced by the border lines of crystal planes (Grain-boundary induced melting, GBI) [6,7]. Unlike the KTHNY theory, here the phase transition is of the first order and normally goes without the formation of the additional phase. The mentioned borderlines represent the long arrays of dislocations with the same Burgers vectors. Such a disorder in the structure can be treated as two crystalline planes rotated by some angle relative to each other [8].
Another theory predicting one-step first-order phase transition was suggested in the paper [9]—so-called density wave theory. This approach predicts the change of entropy and the magnitude of the first peak of structure factor, which agree well with the results of the numerical simulation. Nevertheless, this theory does not take into account fluctuations leading to the loss of the positional long-range order, so that it cannot fully describe the character and the order of the phase transition.

As the KTHNY theory appeared, it has been thoroughly studied in the systems with various pair interaction potentials. The first structures to explore were hard-sphere (discs) systems, the systems with Coulomb and Lennard–Jones interaction potentials. In the last years, the structures with dipole-dipole interactions and Debye–Hückel (Yukawa) potential are actively studied, as the experimental investigations of colloidal suspensions and dusty plasma made a huge step forward [10].

In the last thirty years, many experimental and numerical works on classical monolayer (two-dimensional) systems were published; however, their results are significantly diverging. A first-order phase transition was observed in numerical simulation of the systems with various interparticle interaction potentials [11–13], and also in experiments [14,15]. One-step continuous phase transition was detected in dusty plasma experiments [15–18], in the system of hard discs [19] and others [11,20].

Two-step continuous phase transition consistent with KTHNY theory was observed in numerical simulation of dusty plasma structures [21,22], in experiments and simulations of colloid structures [23–27] and others [28–30]. At present, there are only a few experiments in dusty plasma structures, where the two-step phase transition would be registered. We should mention the works [31] and [4], where the melting of two-dimensional dusty plasma structures in high-frequency rf-discharge was studied experimentally.

It should also be noted that, based on the numerical simulation results, the authors of [10] came to a conclusion that the existence and stability of the hexatic phase in simulated systems depend not only on the number of particles in simulated systems, but mostly on the choice of the time interval for the stability to be achieved.

As the results presented in cited literature are obviously inconsistent, the issue of the scenario of phase transitions in two-dimensional systems is still open.

2. The determination of the phase state of two-dimensional systems

For the qualitative and quantitative analysis of the phase state of 2d-systems, the spatial correlation functions are usually used (pair $g(r)$ and orientational $g_6(r)$) [5,10,32–37]. It should be noted that in the work [36] the behavior of $g_6(r)$ function is presented, including the vicinity of the points of phase transitions in dissipative Yukawa systems with $\nu_{fr} \neq 0$ (where $\nu_{fr}$ is the friction coefficient of particles due to their collisions with the neutrals of surrounding gas). According to KTHNY theory, the function $g_6(r)$ for the crystal tends to the constant value on distances $r$ larger than $4 - 6 \nu r_p$, and for the hexatic phase the asymptotics of $g_6(r)$ follows the power-law function $r^{-1/5}$. The form of the orientational correlation functions remained unchanged within each phase of the structures under study, and their magnitude was fully determined by the number of the originating topological defects. As a consequence, the normalized functions $g_6^* = g_6(r)/N_6$ formed three groups of curves, corresponding to the different phase states of the system: crystal, hexatic and liquid (see figure 1): here $N_6$ is the relative number of particles with six nearest neighbours.

It is usually assumed that in case of KTHNY scenario, both phase transitions in the system are of the second order [8]. Nevertheless, the results of some numerical and theoretical studies show that, depending on the type of pair interaction potential, both transitions could be of the first order, or one of them can be of the first, and the other—of the second order [10,38,39].
3. Thermodynamic properties of Yukawa systems

In the present work we show the results of the numerical study of thermodynamic properties of strongly coupled liquid and crystalline 2d-systems of particles which interact via the screened Coulomb (Yukawa) potential $\phi(r) = (eZ)^2 \exp(-r/\lambda)/r$, where $\lambda$ is the screening length, $eZ$ is the charge of a grain. The coupling parameter $\Gamma^* = 1.5(eZ)^2(1 + \kappa + \kappa^2/2) \exp(-\kappa)/(Tr_p)$ (where $\kappa = r_p/\lambda$, $T$ is the temperature of the particles measured in energy units, and $r_p$ is the mean interparticle distance) was varied within the wide range, and its discretization interval was chosen to be small enough to disambiguate the behavior of the system close to the points of phase transitions.

The numerical simulation was carried out by the Langevin molecular dynamics method (using the periodic boundary conditions in two chosen directions), based on the solution of the system of $N_p$ ordinary differential equations, $N_p$ being the number of the independent particles in computational cell. The stochastic character of motion of the particles with the given kinetic temperature $T$ was determined by the Langevin force $F_{ran}$. The simulation technique is detailed in [33]. The calculations were carried out for the homogeneous 2d- Yukawa systems with the values of screening parameter $\kappa \equiv r_p/\lambda = 1, 1.5, 2, 3, 4$ (where $r_p = (N_p/S)^{1/2}$, and $S$ is the area of the computational cell). The number of independent particles in the central computational cell $N_p$ was varied from 256 to 4096. Dependent on the number of particles, the cut-off length of potential $r_{cut}$ changed from $5r_p$ to $25r_p$. The majority of data were obtained for $N_p = 1024$ independent particles and $r_{cut} = 12r_p$, because the further increase of the number of particles did not lead to the substantial change of the numerical results.

The internal energy was calculated by the expression

$$U = \frac{m}{2} T + (m - 1) \pi n \int_0^\infty \phi(r) g(r) r^{m-1} dr,$$

based on the computations of the pair correlation functions, $g(r)$. The calculations of the $g(r)$ functions were carried out after the system had reached the equilibrium condition, which was controlled by the comparison of the velocity distribution function with the Maxwell function for a given temperature.

The calculations of thermodynamic characteristics ($U$, $C_V$, $S$) vs. $\Gamma^*$, using the obtained $g(r)$ functions, are presented in figures 2–4 for various screening parameters, $\kappa$. 

Figure 1. Normalized functions $g^*_6$ for the crystal phase—$\Gamma^* \sim 165$ (1), for the hexatic phase—$\Gamma^* \sim 140$ (2) and $\Gamma^* \sim 110$ (3), for the liquid phase—$\Gamma^* \sim 85$ (4) and $\Gamma^* \sim 5(5)$. 

Figure 2—3. Thermodynamic properties of Yukawa systems

[Graphs not visible in text format]
Figure 2. The averaged values of $\delta U$ (bold solid line) vs. $\Gamma^*$ for 2d-Yukawa systems with various $\kappa = 1.4$.

Figure 3. The $(C_V - 1)$ values vs. $\Gamma^*$ for 2d-Yukawa systems (solid line), obtained from the averaged $\delta U$ values. Dotted curves are the lines of phase transitions.

Figure 4. The excess entropy $\Delta S$ vs. $\Gamma^*$ for 2d-Yukawa systems, obtained from the averaged $\delta U$ values.

The illustrations of normalized functions $U(\Gamma^*)$, averaged by $\kappa$ and $\xi$ ($\xi = 2(\epsilon Z)^2(1 + \kappa + \kappa^2/2)\exp(-\kappa)/(\nu_p^3\pi M)1/2/\nu_f$, are presented in figure 2. It can be easily seen that the obtained normalized values of $\delta U = (U - U_o - mT/2)/T$ are completely determined by the value of $\Gamma^*$. Note that all the numerical curves ($\delta U, V, S$) have the singularities close to $\Gamma^* = 98$ (point of inflexion) and close to $\Gamma^* = 154$ (jump). As in the systems with a constant volume the criterion
of the first-order phase transition is the jump of the specific entropy of the system, and the criterion of the second order phase transition is the jump of its derivatives with respect to the temperature and the pressure, we can state that the phase transition observed in the proximity of $\Gamma^* = 98$ is of the second order, and $\Gamma^* = 154$ is the phase transition of the first order.

The finiteness of the peak on $C_V$ curve near the solid-hexatic transition and the difference between the observed jump of the $C_V$ value near the fluid-hexatic transition from the classic Heaviside step function, as well as the smoothed features of the curve $\Delta S(\Gamma^*)$, are obviously caused by the mathematical peculiarities of integration/differentiation of discontinuous data. The rougher is the discretization of analyzed data, the wider is the observed peak, the smaller is its amplitude, and the singularities obtained by the integration become less distinctive.

4. The comparison of the numerical results with the existing simulation and experimental data
The comparison of the phase transition points from papers [37, 38, 40, 41] to the results of the present work is shown in figure 5. In [38], the temperature dependence of the internal energy of the system $U(T)$ was analyzed, and the assumption made for the first time that the transition liquid-hexatic is close to the continuous one, and the transition hexatic-crystal has the evidences of the first-order transition. In papers [37, 40, 42] the point of liquid-hexatic phase transition was found from the analysis of the orientational correlation function $g_6(r)$. The hexatic-solid phase transition was found in [41] from the Lindemann criterion on the curve where $D \to 0$. Note that the authors of [40] claim that the formation of the perfect crystal (where $D \to 0$) takes place when $\Gamma^* \approx 118.5$, and the authors of [42] state that the critical value is $\Gamma^* \approx 108$. The reason could be the insufficient quantity of particles in the simulation or/and too short observation time to correctly analyze the spatial behavior of orientational correlation function $g_6(r)$.

5. The dependence of existence of the hexatic phase on the concentration of particles in the system
In most of the experiments studying the phase transitions in colloidal systems the concentration of particles is a variable factor. According to the existing experimental data on colloids, the

![Figure 5. Phase diagram for the Yukawa systems according to the data from [37, 38, 40, 41]: the dependence $\Gamma^*$ on $\kappa = 0.6$: (▲; △) — [38], (□) — [40], (○) — [37], (◊) — [41], (■) — [42].]
formation of the hexatic phase can be observed within the wide range of particles concentration: from ~ 5–10% [43] to ~ 30% [2].

In figure 6 one can see the dependence of \( l_p^g/l_p^c \equiv \kappa^g/\kappa^c \) on \( \kappa^c \) (where \( l_p^c(g) \) and \( \kappa^c(g) \) are the mean interparticle distance and the screening parameter on the lines of formation of crystal \( (c, \Gamma^c_*=154) \) and hexatic \( (g, \Gamma^g_*=98) \) phases, respectively) for Yukawa systems with the constant screening length \( \lambda \), temperature and charge \( Z \) of the particles. It is easy to see that under the given conditions the range of concentrations \( l_p^2 \), corresponding to the region of existence of the hexatic phase, varies from ~ 10% to ~ 30% while \( \kappa^c \) changes from 9 to 4. However, one should keep in mind that real colloidal solutions are self-consistent systems; hence, every change in the concentration or the temperature of a system could modify charges of the particles and their screening lengths.

6. Conclusion
We have presented the results of numerical investigation of thermodynamic functions and characteristics, such as the internal energy, the entropy and the specific heat, for strongly coupled liquid and crystal systems of the particles interacting via the Yukawa potential. The simulations were carried out for the two-dimensional structures within the wide range of parameters corresponding to the conditions of experiments in the laboratory dusty plasma. The mentioned thermodynamic characteristics have two singularities within the melting of the considered systems near \( \Gamma^c_*=98 \) and \( \Gamma^g_*=154 \). The behavior of the thermodynamic characteristics close to these points shows that the phase transitions observed in their proximity are of the second and of the first order, respectively, which can be considered as one more evidence of the two-stage melting scenario of two-dimensional Yukawa systems. The results were compared to the existing experimental, numerical and analytical data. The dependence of the position of the melting lines and the range of existence of the hexatic phase on the concentration of the grains in the considered system was studied.

The results of the present work may be easily adapted for the systems with the wide range of isotropic pair potentials that are interesting in plasma physics as well as in the medicine, biology, physics of polymers and other colloidal systems.
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