Melting of small clusters with Yukawa interaction potential

X G Koss, O F Petrov, M I Myasnikov, K B Statsenko and M M Vasiliev

Joint Institute for High Temperatures of the Russian Academy of Sciences, Izhorskaya 13 Bldg 2, Moscow 125412, Russia
E-mail: Xeniya.Koss@gmail.com

Abstract. In present work, the results of the numerical simulation of the dynamics of two-dimensional clusters of 7 and 18 particles interacting via the Yukawa potential are presented. The simulation was carried out by the Langevin molecular dynamics method. We have numerically obtained the MFPT entropy functions for the systems of 7 and 18 particles for the various values of kinetic temperature, corresponding to the conditions of the laboratory experiments with gas-discharge dusty plasma. Three phase states of the considered small systems are registered: crystal, liquid and transitional. The mechanism of phase transitions in the systems under study is described. The suggested technique of the analysis of the system dynamics can be applied to the structures as small as desired.

1. Introduction

Physical properties of dynamical objects are often strongly dependent on the size of the structure. The properties of small structures are important in various fields of science and technology, especially in nanoindustry, as nanomaterials and crystal grains can be considered as small systems. Fullerenes and other quasi-two-dimensional carbon-based cluster structures open up new possibilities for the development of nanoelectronic technologies. As clusters consisting of several dozens of particles can retain their individual properties inside macroscopic objects, it makes it possible to design new materials with unique qualities. Clusters display the properties that are characteristic neither for microscopic, nor for macroscopic bodies. That is why these mesoscopic objects can be treated as the “fifth state of matter” in addition to the solid, liquid, gaseous and plasma states.

Small systems are strongly unhomogeneous—one can hardly distinguish their superficial properties from the volumetric ones. That is the reason why the diagnostics of their condition considerably differs from the diagnostics of the macroscopic objects, and both theoretical and experimental studies of their properties are quite a serious challenge. However, there is a unique physical object that provides an opportunity to observe mesoscopic systems with a naked eye and to register the motion of their components on the “kinetic” level—it is the dusty plasma system.

The dusty plasma is an ionized gas containing micron-size charged condensed grains (dust). The most of experimental investigations of dusty plasma properties are performed in weakly ionized plasma of gas discharges. Here non-emitting particles gain the negative charge, which
amounts to $e Z_p \sim 10^3 - 10^5 e$ [1, 2]. The combined effect of the interaction between dust grains and dissipative processes in this plasma can lead to the formation of dust structures (similar to a liquid or to a solid), or to the complex oscillatory or chaotic regimes [3–9].

One of the most interesting and important questions in the properties of small systems is the study of their phase states and transitions. Nevertheless, the classical thermodynamic approach is not applicable for this task. The fact is that the key concept in classical thermodynamics is the thermodynamic limit, i.e. the transition to the system consisting of the unlimited number of particles in the unlimited volume; apparently, this transition cannot be performed in mesoscopic structures [10]. For this reason the local structure of these systems becomes very important, because it is the source of information about other equilibrium properties. However, we cannot use the distribution functions for such unhomogeneous objects, as even one-particle distribution functions strongly depend on the spatial position of particles.

A great help here could be the methods of analysis of dynamical systems, particularly, the “dynamic entropy”. The concept of dynamic entropy was introduced by Shannon [11] and developed later by Kolmogorov [13]. The dynamic entropy of Kolmogorov–Sinai is the sum of positive Lyapunov exponents [14, 15], that are the measure of the exponential divergence of the neighbour trajectories in the phase space, i.e. the instability of the system evolution. This quantity is the measure of “complexity” of a dynamical system [16]. The value of the dynamic entropy decreases as the system becomes more ordered, when the development of the phase space becomes more difficult [17, 18]. So, the dynamic entropy decreases when, e.g., the liquid crystallizes or the degree of magnetization of the system increases [18–21].

Nevertheless, the calculation of the Kolmogorov–Sinai entropy has its difficulties, especially in cases when it is small, and a long time is needed for its calculation [19, 22]. Not long ago, the generalization of a concept of the dynamic entropy was proposed, combining the microscopic description of the dynamical system and macroscopic stochastic description of the fluid dynamics. This generalization takes into account the fact that the amount of information needed for the description of the ways of the stochastic process is strongly dependent on the spatial scale $\varepsilon$.

To calculate the dynamic entropy, in the present work we use the simple approximation which can be easily used for the analysis of experiments as well as for the numerical simulation [22–24]. If the spatial scale $\varepsilon$ is not very small [22], one can estimate the dynamic entropy by drawing up the sphere of radius around the particle in the moment $t = 0$, and then finding the moment of time $\tau$, when the trajectory first passes the threshold value $\varepsilon$. Averaging this mean first-passage time, MFPT, $\tau(\varepsilon)$ over all the particles of the system, we obtain the “MFPT dynamic entropy” $S(\varepsilon)$ [23]:

$$S(\varepsilon) \equiv 1/\tau(\varepsilon),$$

where $\tau(\varepsilon) = \int_0^\infty P_\varepsilon(t) dt$, and $P_\varepsilon(t) dt$ is the probability of the particle to reach the border of the sphere $\varepsilon$ in the moment of time between $t$ and $t + dt$. So, the dynamic entropy $S(\varepsilon)$ shows how fast the particle leaves its environment [25].

2. Parameters of the numerical simulation

The simulation of the small systems was performed with the Langevin molecular dynamics method, based on the solution of the system of $N_p$ ordinary differential equations of motion (where $N_p$ is the number of particles in the calculation cell), taking into account the Langevin force. This force is responsible for the stochastic character of the grain motion and for their equilibrium kinetic temperature. The simulation technique is detailed in [26]. The calculations were carried out for the two-dimensional Yukawa systems.

We have simulated clusters consisting of 7 and 18 particles. The radius of the particle was $a = 5 \times 10^{-4}$ cm, the density of the material of the particle—$\rho_d = 1.5$ g/cm$^3$, the mass of a
paricle—$7.854 \times 10^{-10}$ g, its charge $q_d = 1.5 \times 10^4 e$. The particles were confined by the electrical field of a trap with the frequency $\omega = 10 \text{ s}^{-1}$. The friction coefficient associated with the collisions of the particles with neutrals of the buffer gas was set $10 \text{ s}^{-1}$, the screening length—0.01 cm. The kinetic temperature of the dusty subsystem was given $T = 2, 5, 10, 30 \text{ eV}$, in the range typical for the experiments in gas discharges of laboratory plasma [26]. The time step of the simulation was set equal to 0.01 s, and the whole time of the simulation—400 s.

3. Analysis and discussion of results

With the help of the numerical simulation, we have obtained the dependences $S(\varepsilon) \equiv 1/\tau(\varepsilon)$ for various values of the kinetic temperature in the systems consisting of 7 and 18 particles. The results obtained for the systems under study with various temperatures, are shown in figures 1–3. The beginning of the curves (points with small $\varepsilon$) corresponds to the ballistic regime of particle motion. It can be easily seen that the motion of all particles of the system is identical.

![Figure 1](image-url)

**Figure 1.** The dynamic entropy for the clusters of 7 (a) and 18 (b) particles with the temperature 2 eV. The insets show the trajectories of particles’ motion for 40 seconds.
Figure 2. The dynamic entropy for the clusters of 7 (a) and 18 (b) particles with the temperature 5 eV. The insets show the trajectories of particles’ motion for 40 seconds.

in this regime. The difference in the behavior of curves becomes visible and significant for large values of $\varepsilon$ (after the bend of a curve). For the systems in crystalline state (small temperatures), the function of dynamic entropy drops abruptly after the bend point and goes to the zero. The value of $\varepsilon$, when $S(\varepsilon) = 0$, corresponds to the size of a “cage”, where every particle of a system “lives”. It describes the situation where the motion of each particle of a system is spatially bounded. When the temperature rises, the “bunch” of curves begins to separate after the bend point that corresponds to the various characters of motion of the particles in different parts of a structure. Note that the cluster of charged particles in external cylindrical electrical field has the circular symmetry; namely, it consists of several “shells” centered around one particle (see, e.g., the insets in figures 1a and 1b). The particle in the center of the structure is the most confined one, and its motion is reflected by the most abrupt graph in the bunch. Curves with the smaller angle of slope correspond to the displacement of particles belonging to the next shell of the cluster. For the systems with larger temperatures, the part of the bunch after the bend point becomes integrated again (see figure 3); this situation corresponds to the diffusive regime.
Figure 3. The dynamic entropy for the clusters of 7 (a) and 18 (b) particles with the temperature 30 eV. The insets show the trajectories of particles’ motion for 40 seconds.

of motion of the particles.

Therefore, the melting scenario in the systems studied is the following. As the temperature rises, the outer shell of a cluster is the first to melt—it can be seen by the increasing of the size of “cages”, where the particles of the outer shell “live”. As a result, the depth of the potential well, where the particles of the outer shell move, decreases; it causes the reduction of the potential well of the shell nearest to the outer. On the next step, as the temperature continues to rise, the second shell melts. The dynamic entropy graphs for these two shells merge. If the system is being heated further, the chain reaction takes place: the shells melt one after another, from the edge to the center of the system, until the whole structure becomes liquid, and the bunch of the dynamic entropy curves merges. This scenario is illustrated in figure 4, where the mean kinetic energies of particles in different shells are shown.
Figure 4. Normalized mean kinetic energy of particles in different shells of a cluster consisting of 18 grains. “Shell 1”—central particle, “shell 2”—middle shell, “shell 3”—outer shell of a cluster.

4. Conclusion
In present paper, the MFPT dynamical entropy functions were obtained in numerical simulation for the clusters of 7 and 18 particles. The kinetic temperature of the system under study was varied in the range corresponding to the conditions of laboratory dusty plasma experiments. Three phase states of the considered small systems were observed—crystal, liquid and transitional. The mechanism of phase transitions in the systems under study is described. The suggested technique of the analysis of the system dynamics can be applied to the structures as small as desired, down to one particle.

Acknowledgments
This work was supported by the Russian Science Foundation (project No. 14-12-01440).

References
[1] Sodha and Guha S 1971 Adv. Plasma Phys. 4 219
[2] Rosenberg M and Mendis D A 1995 IEEE Trans. Plasma Sci. 23 177
[3] Thomas H, Morfill G, Demmel V et al. 1994 Phys. Rev. Lett. 73 652
[4] Melzer A, Trottenberg T and Piel A 1994 Phys. Lett. A 191 301
[5] Fortov V E, Nefedov A P, Petrov O F, Samarian A A and Chernyschev A V 1996 Phys. Rev. E 54 R2236
[6] Vaulina O S, Vladimirov S V, Repin A Yu et al. 2006 Phys. Plasmas 13 012111-1–5
[7] Zhukhovitskii D I 2015 Phys. Rev. E 92 023108
[8] D’yachkov L G 2015 Tech. Phys. Lett. 41 602
[9] D’yachkov L G 2015 High Temp. 53 613
[10] Gross D H E. 2001 Microcanonical Thermodynamics (Singapore: World Scientific)
    Hill T L 1987 Statistical Mechanics: Principles and Selected Applications (N.Y.: Dover Publications)
[11] Shannon C E 1948 Bell Syst. Tech. J. 27 379
[12] Shannon C E 1948 Bell Syst. Tech. J. 27 623
[13] Kolmogorov A N 1959 Dokl. Akad. Nauk USSR 124 754
    Sinai Y G 1959 Dokl. Akad. Nauk USSR 124 768
[14] Pesin Ya B 1977 *Russ. Math. Surv.* **32** 55
[15] Livi R, Politi A and Ruffo S 1986 *J. Phys. A* **19** 2033
[16] Kolmogorov A N 1983 *Russ. Math. Surv.* **38** 29
[17] Cleary P W 1989 *J. Math. Phys.* **30** 689
[18] Butera P and Caravati G 1987 *Phys. Rev. A* **36** 962
[19] Dellago Ch and Posch H 1996 *Physica A* **230** 364
[20] Caiani L, Casetti L, Clementi C and Pettini M 1997 *Phys. Rev. Lett.* **79** 4361
[21] Wales D J. and Berry R S 1991 *J. Phys. B* **24** L351
[22] Gaspard P and Wang X-J 1993 *Phys. Rep.* **235** 291
[23] Allegrini P, Douglas J F and Glotzer S C 1999 *Phys. Rev. E* **60** 5714
[24] Gaspard P, Briggs M E, Francis M K, Sengers J V, Gammon R W, Dorfman J R and Calabrese R V 1998 *Nature* **384**, 865
[25] Gaspard P and Nicolis G 1990 *Phys. Rev. Lett.* **65** 1693
[26] Fortov V E and Morfill G E (ed) 2010 *Complex and Dusty Plasmas* (CRC Press)