GENERAL PROBLEMS OF THEORETICAL PHYSICS

CELLULAR STRUCTURES IN A SYSTEM OF INTERACTING PARTICLES

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The general description of the formation of a cellular structure in the system of interacting particles is proposed. The analytical results for possible cellular structures in the usual colloidal systems, systems of particles immersed in a liquid crystal, and gravitational systems have been presented. It is shown that the formation of a cellular structure in all systems of interacting particles at different temperatures and concentrations of particles has the same physical nature.

For a long time, the resulting physical properties of systems of interacting particles have been the subject of much active researches. The phase transitions and the ordering of a many-particle system and its properties are of fundamental importance for physics and wide practical applications. In order to describe the behavior of a many-particle system with different strengths and characters of the interaction, it is necessary to possess a method which would take a spatial inhomogeneous distribution of particles into account. That is, such a method should consider the formation of clusters, cellular structures, and less ordered structures. Basically, the statistical description of many-particle systems concerns homogeneous states. But the most interesting and challenging problem in condensed matter physics involves the study of phase transitions with the formation of a spatially inhomogeneous distribution of particles, clusters or cellular structures. These structures were observed in usual colloids [1,2], a system of particles introduced in a liquid crystal [3–5], and even in galactic systems [6]. As evident from these examples, the formation of a cellular structure in the system of interacting particles has no essential dependence on the strength and character

of the interaction and can occur in different physical situations. It is worth noting that the appearance of a cellular structure changes dramatically the properties of condensed matter. Depending of the size of particles, both the reversible and irreversible clusterings are observed. During the past decade, colloidal systems have been used as a model system to understand the phenomenon of two-dimensional melting transition. In usual colloids, the crystal-like ordering, including the formation of a hexagonal crystal structure, was observed [7]. Experimentally, it was found that, at the initial stage, a cellular structure originates from a region with the lowest local density of particles. In all cases, the existing elastic interaction leads to a spatially inhomogeneous distribution of particles with the formation of regions free from particles. The cellular structure realizes a minimum of the free energy and leads to the stabilization of the formed regions in a pure elastic medium, so that the particles are placed at the boundaries of those regions. To describe the conditions of the formation and the properties of these particle structures, one should take into account all aspects of the particle interaction.

The present work is devoted to the study of necessary conditions of the formation of cellular structures in an arbitrary system of interacting particles. First, we give the general thermodynamical description of the formation of regions which are free from particles at any character and strength of the interaction. Then, by the example of ordinary and liquid-crystal colloids, we will show how a phase transition of the first kind with the formation of a spatially inhomogeneous distribution of particles can be realized. We will define the conditions

(temperature, concentration, and interaction strength), under which a cellular structure can appear in the system. The formation of such structures corresponds to the minimum of the free energy, whose form will be obtained from the first principles.

Let us consider firstly a system of noninteracting particles and determine conditions of the formation of a void (a region which is free from particles) under their homogeneous distribution. Such a problem was first solved in [6] in the case of a homogeneous distribution of particles with concentration c. It was shown that the probability of the formation of a spherical void of volume V (the form of a void does not play a principal role, and other forms can be treated analogously) is

$$P(V) = \exp(-cV) = \exp(-N), \tag{1}$$

where N is the mean number of particles positioned in the volume V.

We now try to determine the analytical result for the probability of the formation of a void of volume V for a system of interacting particles. To this purpose, we use the formalism of the ground canonical assemble of N particles in volume V at temperature T. The particle distribution can be written in the standard form [10] as

$$W(N) = \exp\left\{\beta\mu N - \beta F\right\}, \tag{2}$$

where $\beta = \frac{1}{kT}$ – the inverse temperature, μ – the chemical potential, and $F(N, V, T)$ – the free energy which can be calculated with the help of a canonical assemble. With this probability, we find the mean value of the quantity $exp(qN)$ which depends on the number of particles as

$$\langle \exp(qN) \rangle = \sum_N \exp(qN)W(N) =$$

$$= G^{-1} \sum_N \exp\{(\beta\mu + q)N - \beta F\} \equiv$$

$$\equiv \exp\{\Psi(\beta\mu + q) - \Psi(\beta\mu + q)\}. \tag{3}$$

Here, we have used the well-known relation between the statistical sum of the ground canonical assemble G and the thermodynamic potential

$$\ln G(\mu, V, T) = \frac{PV}{kT} \equiv \Psi(\mu, V, T). \tag{4}$$

This formula can be presented as

$$\sum_N z^N W(N) = \exp\left\{\Psi(z\exp(\beta\mu)) - \Psi(\exp(\beta\mu))\right\} =$$

$$= \exp(-\Psi)\exp(\Psi(z\exp(\beta\mu))). \tag{5}$$

We now expand the right-hand side of this relation in a series in z. By comparing the terms with the same powers of z in both parts of the equality, we obtain

$$W(N) = \exp(-\Psi)\frac{\exp(\beta\mu)}{N!}(\exp\Psi)_0^N, \tag{6}$$

where

$$(\exp\Psi)_0^N = \left[\left(\frac{d}{d(z\exp(\beta\mu))}\right)^N \exp\Psi(z\exp(\beta\mu))\right], \tag{7}$$

when $z\exp(\beta\mu) = 0$. After this operation, we can obtain the probability to find an empty void in the system of interacting particles:

$$W(0) = \exp\left(-\frac{PV}{kT}\right). \tag{8}$$

It is seen that this probability depends on the equation of state. Switching off the interaction in the system of particles leads to the above-presented result of the Poisson distribution.

Formula (8) is quite representative. If we remember that the Laplace pressure of a bubble is $P = \frac{2\sigma}{R}$, where R is the bubble radius, and σ is the surface tension of the bubble, we can rewrite the probability in the form

$$W(0) = \exp\left(-\frac{8\pi\sigma R^2}{3kT}\right) \tag{9}$$

which is identical to the probability of the formation of a bubble of the new phase at a first-order phase transition. Thus, the probability of the formation of a region without particles is determined by the equation of state of the system of interacting particles, as if they were present in the given region. In addition, the formation of a void depends on the formation of a boundary similarly to the case of a first-order phase transition. These remarks are a weighty argument testifying to the correctness of the proposed approach to the determination of the probability of the formation of a void without particles.

Now, we will analyze the thermodynamic properties of a system of weakly interacting particles. In the general

case, the equation of state can be written in the standard form

$$\frac{PV}{kT} = N(1-b),\tag{10}$$

where b is the virial coefficient. For a gas of hard spheres, the equation of state looks as

$$PV = kTN\frac{1+\nu+\nu^2-\nu^3}{(1-\nu)^3},\tag{11}$$

where $\nu = \frac{NV_0}{V}$ is the packing factor. In the case of the system of particles which interact with one another through a short-range repulsive potential as hard spheres and by the gravitation force at large distances, the equation of state can be written in the limit of a low packing factor as

$$PV = kTN + 1/2N^2\left(Uv - \frac{W_G v^{1/3}}{2N^{1/3}}\right).\tag{12}$$

All above-given equations of state are of the van der Waals type. Having known the equation of state, we can obtain the probability of the existence of a void without particles and evaluate the mean value of the void radius as the distance, where the probability decreases by a factor of e. In the case of noninteracting particles, we can write $cV = 1$ or the number of particle in this void is $N = 1$. Thus, in the system of noninteracting particles, one cannot form the voids without particles! For the system of weakly interacting particles, we can use the equation of state in the standard form. In this case, the void volume of cavity can be estimated by the relation

$$\frac{PV}{kT} = N(1-b) = 1\tag{13}$$

or by $(\frac{NV_0}{V})\frac{V}{V_0}(1-b) = 1$,

$$V = V_0\frac{1}{\nu(1-b)},\tag{14}$$

where V_0 is the volume of one particle, and ν is the packing factor. If $\nu \sim 1$ and $b \ll 1$, we may assert that the voids in the system with weak interaction cannot be formed. The size of a void will be smaller than the size of a particle. If the packing factor decreases and the interaction energy increases, the formation of regions without particles becomes possible, and the size of a void can be evaluated by the previous formulas. For example, if $\nu \sim 0.5b$ or less and $b = 0.5$, we obtain that $V \sim 3V_0$ or more.

The following example is a gas of hard spheres. In this case, particles interact through the short-range repulsion, and the equation of state yields

$$V = V_0\frac{(1-\nu)^3}{\nu(1+\nu+\nu^2-\nu^3)}.\tag{15}$$

If $\nu \to 1$, we have $V \to 0$. In this case, the close packing is realized, and no voids can be formed in this system. If $\nu \to 0$, we get $V = V_0\frac{1}{\nu}$, and the formation of voids is possible according to the assumptions made above. Thus, the formation of voids is completely defined by the interaction strength and the concentration of particles. If the interaction of particles becomes stronger, i.e., if the ratio of the potential and kinetic energies grows, we cannot use the description of the system in terms of the virial expansion and must use only the equation of state.

In the process of aggregation, many voids (cells) can be produced. Let us estimate their number in the general case. If m cells in the volume $\overline{V}$ arise in the process of aggregation, the following relation must hold:

$$mV + NV_0 = \overline{V}.\tag{16}$$

This relation yields

$$m = \frac{\overline{V}}{V} + N\frac{V_0}{V}.\tag{17}$$

With regard for the previous relation between V and V_0, the number of cells is

$$m = N\frac{1-b_2}{\ln 2}(1-\nu).\tag{18}$$

In view of this relation, we can conclude that the number of cells without particles increases with decrease of both the packing factor ν and the interaction energy. If the packing factor $\eta \to 1$, which corresponds to the crystal structure, the number of voids goes to zero. If we consider the system of noninteracting particle, $b_2 \to 0$, and we obtain $m = N(1-\nu)$ which depends only on the packing factor.

In the general case of interacting particles in order to demonstrate the mechanism and the character of a phase transition accompanied by the formation of an inhomogeneous distribution of particles, we write the free energy of particles in an ordinary colloidal system in the approximation of self-consistent field in the form [8,9]

$$F = F_p + F_s + F(n),\tag{19}$$

where the first term

$$F_p = \int U(\mathbf{r}-\mathbf{r}')f(\mathbf{r})f(\mathbf{r}')d\mathbf{r}d\mathbf{r}' + ...\tag{20}$$

is the interaction energy in terms of the spatial distribution function $f(\mathbf{r})$ of particles, and $U(\mathbf{r} - \mathbf{r}')$ is the pairwise interaction energy. The second term

$$F_s = \int \{f(\mathbf{r}) \ln f(\mathbf{r}) + [1 - f(\mathbf{r})] \ln[1 - f(\mathbf{r})] d\mathbf{r} \qquad (21)$$

is the entropy part of the free energy which reflects the fact that two particles cannot occupy the same place in space. The last term of the free energy describes the wetting energy or the coupling between the elastic media and colloidal particles. It can be modeled by

$$F_n = \int f(\mathbf{r}) \sum_i W(\mathbf{R}_i - \mathbf{R}) d\mathbf{r}, \qquad (22)$$

where $W(r)$ contains the information about the microscopic wetting properties of the particle surface.

The requirement for the free energy to be minimum allows us to obtain a self-consistent solution for the distribution function $f(r)$. If the distribution is homogeneous, then, by definition, the mean value of $f(\mathbf{r}) = c$, where c is the relative particle concentration. If the distribution is inhomogeneous, the deviation from the homogeneous distribution can be searched in the form $f(\mathbf{r}) = c \pm \varphi(\mathbf{r})$, where $\varphi(\mathbf{r})$ is a change of the distribution function of particles. Let us pass to the continuum description by using the long-wavelength expansion of the spatial distribution function: $\varphi(\mathbf{r}') = \varphi(\mathbf{r}) + \boldsymbol{\rho}_i \partial_i \varphi(\mathbf{r}) + 1/2\boldsymbol{\rho}_i \boldsymbol{\rho}_j \partial_i \partial_j \varphi(\mathbf{r}) +$. This can be always made, if we are interested in inhomogeneities, whose scale is much more than the size of a particle.

Denoting, by $\boldsymbol{\rho} = \mathbf{R} - \mathbf{R}'$, the distance between two particles, we can present a change of the free energy due to the inhomogeneity of the distribution function of particles in the form

$$\triangle F(\varphi) = \int d\mathbf{R} \left\{ \frac{1}{2} l^2 (\nabla \varphi)^2 - 1/2\mu^2 \varphi^2 + \frac{1}{4}\lambda \varphi^4 - \varepsilon\varphi \right\}, \qquad (23)$$

where

$$\mu^2 \equiv \left(V - \frac{kT}{c(1-c)} \right), \quad V = \int U(\boldsymbol{\rho}) d\boldsymbol{\rho}, \qquad (24)$$

$$l^2 = \int U(\boldsymbol{\rho}) \boldsymbol{\rho}^2 d\boldsymbol{\rho}, \qquad (25)$$

and λ is the coefficient responsible for a nonlinearity of the system which is induced by the many-body

interaction. The coefficient $\varepsilon = N4\pi R_0^2 W$ presents the energy of wetting of particles by the medium, R_0 is the particle size, and W presents the anchoring energy of molecules of the medium with the surface of a particle. To solve the problem on the inhomogeneous distribution of particles, we consider the normalization relation $\int f(\mathbf{r}) d\mathbf{r} = N$, $\int \varphi(\mathbf{r}) d\mathbf{r} = 0$.

In this case, the expression for the free energy coincides with that describing a first-order phase transition which is accompanied by the formation of clusters. The temperature of such phase transition to a new state with inhomogeneous distribution of particles is determined by the relation

$$kT_c = c(1-c)V. \qquad (26)$$

The functional of the free energy should be minimal, i.e., $\triangle\varphi - \frac{dV}{d\varphi} = 0$, where $V = -1/2\mu^2\varphi^2 + \frac{1}{4}\lambda\varphi^4 - \varepsilon\varphi$ can be used as the potential energy. In the case where the difference of minimum effective potential values is greater than the barrier height, the free energy of one cluster is given by the expression

$$\Delta F = 4\pi \int_0^\infty r^2 dr \left\{ 1/2 \left(\frac{d\varphi}{dr} \right)^2 + V(\varphi) \right\} =$$

$$= -\frac{4\pi}{3} r^3 \varepsilon + 4\pi r^2 \sigma, \qquad (27)$$

where $\sigma = \int_0^\infty d\varphi \sqrt{2V(\varphi)}$ is the surface energy of a cluster corresponding to the solution of the one-dimensional problem. The cluster radius can obtain by minimizing the free energy. It is given by $\widetilde{R}_0 = \frac{2\sigma}{\varepsilon}$. As is well known, can obtain that $\varepsilon = \frac{2\mu\in}{\lambda^{1/2}}$ and $\sigma = \frac{\mu^3}{3\lambda}$. Then $R = \frac{\mu^2 l}{3\lambda^{1/2}\varepsilon}$, and the effective variation of the free energy due to the formation of a cluster is $\Delta F = \frac{8\pi\sigma R^2}{3}$. The probability of the formation of one cluster can be written in the standard form as

$$P(\widetilde{R}) = \exp\left(-\frac{\Delta F}{kT} \right) = \exp\left(-\frac{8\pi\sigma R^2}{3} \right). \qquad (28)$$

Now, we can assert that the formations of a cluster of the new phase, where the concentration of particles is greater than the mean one, and a region free from particles are of the same nature. A cluster possessing the greater concentration and a pore in the system of interacting particles are formed by the interaction of particles [8, 9]. At the relative concentration of particles greater than $1/2$, the pores in a continuous distribution of particles will be formed. But if the relative concentration is less than $1/2$, one will observe

clusters and the free space. The relationship between the regions occupies by particles and those free from particles depends on the concentration of particles and the strength and character of their interaction so as it is allowed by the equation of state. The conditions for the formation of a spatially inhomogeneous distribution of particles correspond to those of the formation of clusters. If the concentration of particles grows, many small clusters form one fractal cluster which will fill all the free space, so that one can observe cellular structures between aggregates of particles. Thus, we have presented the consistent description of cellular structures in systems of interacting particles with regard for the strength and the character of their interaction.

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КОМІРЧАСТІ СТРУКТУРИ В СИСТЕМІ ВЗАЄМОДІЮЧИХ ЧАСТИНОК

Б.І. Лев

Р е з ю м е

Запропоновано узагальнене описання формування комірчастих структур в системі взаємодіючих частинок. Умови формування комірчастих структур визначено з термодинамічних характеристик системи. Для звичайних та рідкокристалічних колоїдів ґрунтуючись на характері та величині взаємодії, визначено температуру та концентрацію частинок, при яких можливе формування комірчастих структур. Пояснено причини формування комірчастих структур в довільній системі взаємодіючих частинок.