Influence of surrounding matter on the properties of clusters is considered by an approach combining the methods of statistical and quantum mechanics. A cluster is treated as a bound \( N \)-particle system and surrounding matter as thermostat. It is shown that, despite arbitrary strong interactions between particles, cluster energy can be calculated by using the controlled perturbation theory. The accuracy of the latter is found to be much higher than that of the quasiclassical approximation. Spectral distribution is obtained by minimizing conditional entropy. Increasing the thermostat temperature leads to the depletion of bound states. The characteristic temperature when bound states become essentially depleted defines the temperature of cluster evaporation. The inverse process of lowering the thermostat temperature, yielding the filling of bound states, corresponds to cluster condensation.

I. INTRODUCTION

The formation of clusters is a common tendency of matter. Clusters of quarks form nucleons, clusters of nucleons form nuclei, clusters of nuclei form atoms and molecules, clusters of the latter form various objects on the Earth, including alive beings. The Earth itself, as well as other planets, are clusters. Planets clusterize around the Sun or around other stars. Galaxies in the Universe are also a kind of clusters.

Generally, a cluster is a compact group of objects bound together for sufficiently long time. More exactly, the lifetime of a cluster is to be much longer than the characteristic times describing its motion as a whole. In the ideal case, when the lifetime of a cluster is infinite, the latter is absolutely stable. Usually, clusters have finite lifetimes, thus, being metastable, although the lifetime can be extremely long.

In what follows, for concreteness, we shall mean under a cluster a group of \( N \) particles forming a bound state because of attracting forces between them. There are two main approaches of treating clusters theoretically, that of statistical and of quantum mechanics. The statistical approach permits to define the relative concentrations of different clusters and other thermodynamic functions of a statistical system, provided that the basic characteristics of each type of clusters, such as mass, binding energy, and quantum numbers, like spin, are given a priori. This approach describes, for example, the relative abundances of chemical elements in the universe [1]. In the droplet models of condensation [1,2] the noninteracting droplets are characterized by their volumes and surface tension. Alternatively, the interaction potentials between droplets are to be postulated [3]. The appearance of droplets is typical of the liquid–vapour phase transition occurring either in usual gases or in nuclear matter [4-6].

Recently, a great attention has been attracted to the use of the statistical approach for describing the deconfinement phase transition in quantum chromodynamics. When increasing temperature or density, hadron matter is expected to decompose into quark–gluon plasma [7-12]. High density of nucleons can be reached in ultrarelativistic nuclear collisions [13-16] and both high density and temperature, in heavy–ion collisions [17-20]. Numerical simulations with lattice models [21-24] undoubtfully show that nonperturbative phenomena dominate in a wide range around the deconfinement phase transition, up to temperatures of about \( 2T_c \) [25,26]. These nonperturbative phenomena are thought to be caused by the formation of quark and gluon clusters [27-32] inside quark–gluon plasma, similar to the appearance of liquid droplets in fog. The deconfinement–confinement phase transition, to our mind, is an analog of the evaporation–condensation phase transition.

In the quantum–mechanical approach, one considers the properties of an individual cluster in the vacuum and the interactions of a small number of clusters. For instance, in last years the properties of multiquark clusters have been intensively studied [33-38]. Such clusters, as various scattering experiments indicate [39-43], can exist in nuclei and even in deuteron [44,45]. More information on multiquark clusters can be found in reviews [46,47]. Other examples of clusters whose description is mainly based on quantum mechanics are nuclei themselves, alpha clusters [48], resonant nuclear clusters [49,50] and metallic clusters [51].

The properties of a cluster, defined when the latter is in the vacuum, can be strongly changed if the cluster is inserted into matter. Moreover, the stability of a cluster can be essentially influenced by surrounding medium. Therefore,
when one calculates the concentrations of clusters in a statistical system, fixing cluster characteristics a priori, while the latter can be noticeably disturbed by the influence of matter, would yield wrong conclusions. At the same time, for understanding how matter influences cluster properties, one needs to have a method of their accurate definition. To describe the properties of a cluster is usually not very easy since one has to deal with bound states of strongly interacting particles.

In the present paper we consider the following mutually related questions: (i) How to accurately calculate the energy spectrum of bound states for an \( N \)-particle cluster? (ii) What are the statistical weights of such states? (iii) How the evaporation or condensation of a cluster is caused by surrounding matter?

The questions addressed above are, of course, too complicated to be exhaustively answered in one paper. Here, we suggest some principal ways of solving the problem and illustrate the ideas by a simplified model: A cluster consists of \( N \) particles interacting with each other through attractive pair forces of power law; surrounding matter is replaced by thermostat. We hope that the suggested approach can be applied to more realistic problems. But first we have to be convinced that there exists the method permitting to answer the above formulated questions in principle.

## II. CLUSTER ENERGY

Consider a system of \( N \) particles defined by the Hamiltonian

\[
H_N = \int \psi^\dagger(\vec{r})K(\vec{r})\psi(\vec{r})d\vec{r} + + \frac{1}{2} \int \psi^\dagger(\vec{r})\psi^\dagger(\vec{r}')\Phi(\vec{r} - \vec{r}')\psi(\vec{r})d\vec{r}d\vec{r}',
\]

in which \( K(\vec{r}) \) is a kinetic–energy operator; \( \psi(\vec{r}) \) is a field operator being a column \( [\psi_n(\vec{r})] \) in the space of internal degrees of freedom, such as spin, isospin and so on. The interaction potential does not depend on internal degrees of freedom.

The average energy of the system can be exactly expressed through the second–order density matrix. There are several forms of such expressions \([52-54]\). In the second–quantization representation, which we use here, the average energy can be written as

\[
\langle H_N \rangle = \frac{1}{2(N-1)} \int \delta(\vec{r}_1 - \vec{r}_1')\delta(\vec{r}_2 - \vec{r}_2')H_2(\vec{r}_1, \vec{r}_2')\times \times \rho_2(\vec{r}_1, \vec{r}_2, \vec{r}_1', \vec{r}_2')d\vec{r}_1d\vec{r}_2d\vec{r}_1'd\vec{r}_2',
\]

where the reduced Hamiltonian is

\[
H_2(\vec{r}_1, \vec{r}_2) \equiv K(\vec{r}_1) + K(\vec{r}_2) + (N-1)\Phi(\vec{r}_1 - \vec{r}_2)
\]

and the second–order density matrix

\[
\rho_2(\vec{r}_1, \vec{r}_2, \vec{r}_1', \vec{r}_2') = \langle \psi^\dagger(\vec{r}_2')\psi^\dagger(\vec{r}_1)\psi(\vec{r}_1')\psi(\vec{r}_2) \rangle.
\]

The form (2) can be easily obtained using the fact that, when the number of particles is fixed, the second– and first–order density matrices are connected by the relation

\[
\int \rho_2(\vec{r}_1, \vec{r}_2, \vec{r}_1', \vec{r}_2')d\vec{r}_2 = (N-1)\rho_1(\vec{r}_1, \vec{r}_1'),
\]

\[
\rho_1(\vec{r}, \vec{r}') = \langle \psi^\dagger(\vec{r}')\psi(\vec{r}) \rangle.
\]

Let us note that there is another way, not mentioned in literature, of deriving (2). Write the Hamiltonian in the Schrödinger representation

\[
H(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) = \sum_{i=1}^{N} K(\vec{r}_i) + \frac{1}{2} \sum_{i \neq j}^{N} \Phi(\vec{r}_i - \vec{r}_j).
\]
Passing to the Heisenberg representation, one transforms the first and second terms in (5) to the first and second terms in (1), respectively. However, nothing prohibits us to rewrite (5) in the identical form

\[ H(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) = \frac{1}{2(N-1)} \sum_{i \neq j}^{N} H_2(\vec{r}_i, \vec{r}_j), \]

in which \( H_2 \) is given by (3). From the latter expression, in the Heisenberg representation we obtain

\[ H_N = \frac{1}{2(N-1)} \int \psi^\dagger(\vec{r}) \psi^\dagger(\vec{r}') H_2(\vec{r}, \vec{r}') \psi(\vec{r}) \psi(\vec{r}') d \vec{r} d \vec{r}'. \]  

(6)

And from (6) one immediately gets (2).

The second–order density matrix (4) can be presented as an expansion

\[ \rho_2(\vec{r}_1, \vec{r}_2, \vec{r}_1', \vec{r}_2') = \sum_{\alpha \beta} B_{\alpha \beta} \Psi_{\alpha}(\vec{r}_1, \vec{r}_2) \Psi_{\beta}^\ast(\vec{r}_1', \vec{r}_2') \]  

(7)

over an orthonormalized basis \( \{ \Psi_{\alpha} \} \). The expansion coefficients, because of the normalization condition

\[ \int \rho_2(\vec{r}_1, \vec{r}_2, \vec{r}_1', \vec{r}_2') d \vec{r}_1 d \vec{r}_2 = N(N-1), \]

obey the sum rule

\[ \sum_{\alpha} B_{\alpha \alpha} = N(N-1). \]  

(8)

With the notation

\[ H_{\alpha \beta} \equiv \int \Psi_{\alpha}^\dagger(\vec{r}_1, \vec{r}_2) H_2(\vec{r}_1, \vec{r}_2) \Psi_{\beta}(\vec{r}_1, \vec{r}_2) d \vec{r}_1 d \vec{r}_2, \]

the average energy (2) becomes

\[ \langle H_N \rangle = \frac{1}{2(N-1)} \sum_{\alpha \beta} B_{\alpha \beta} H_{\beta \alpha}. \]  

(9)

It is natural to choose the basis \( \{ \Psi_{\alpha} \} \) in the expansion (7) as a set of eigenfunctions of the reduced Hamiltonian (3),

\[ H_2(\vec{r}_1, \vec{r}_2) \Psi_{\alpha}(\vec{r}_1, \vec{r}_2) = E_{\alpha} \Psi_{\alpha}(\vec{r}_1, \vec{r}_2). \]  

(10)

Equation (10) describes quantum mechanics of a pair of particles. Such a pair can be called \([54]\) a pairon. Defining

\[ p_{\alpha} = \frac{B_{\alpha}}{N(N-1)}; \quad \sum_{\alpha} p_{\alpha} = 1, \]  

(11)

we see that \( p_{\alpha} \) has the meaning of the probability that a pairon is in a state \( \alpha \). Now, the average energy (9) reduces to

\[ \langle H_N \rangle = \frac{N}{2} \sum_{\alpha} p_{\alpha} E_{\alpha}. \]  

(12)

For concreteness, let us take the kinetic–energy operator in the standard form

\[ K(\vec{r}) = -\frac{\nabla^2}{2m_0}, \]

\( m_0 \) being a particle mass. Then, using the center–of–mass and relative coordinates

\[ \vec{R} \equiv \frac{\vec{r}_1 + \vec{r}_2}{2}, \quad \vec{r} \equiv \vec{r}_1 - \vec{r}_2, \]

3
and introducing the masses
\[ M \equiv 2m_0, \quad \mu \equiv \frac{m_0}{2}, \]
one can, as is known, factorize the eigenfunction in (10) into the product
\[ \Psi_\alpha(\mathbf{r}_1, \mathbf{r}_2) = \Psi_Q(\mathbf{R}) \frac{\chi_{nl}(r)}{r} Y_{lm}(\theta, \phi), \]
in which \( \Psi_Q(\mathbf{R}) \) is a plane wave, with a wave vector \( \mathbf{Q} \), corresponding to a pairon center–of–mass motion; \( Y_{lm} \) is a spherical harmonic; and the pairon relative motion is described by a function \( \chi_{nl} \) satisfying the equation
\[ H_N(r)\chi_{nl}(\mathbf{r}) = E_{nl}(N)\chi_{nl}(r) \tag{13} \]
with the relative Hamiltonian
\[ H_N(r) = -\frac{1}{2\mu} \frac{d^2}{dr^2} + \frac{l(l+1)}{2\mu r^2} + (N-1)\Phi(r). \tag{14} \]
The pairon energy \( E_\alpha \) in (10) reads
\[ E_\alpha = \frac{\mathbf{Q}^2}{2M} + E_{nl}(N). \tag{15} \]

Thus, the pairon quantum index \( \alpha \) is specified as a set \( \alpha = \{Q, n, l, m\} \) of six indices: three components in the wave vector \( Q = \{Q_a | a = 1, 2, 3\} \), each \( Q_a \in \mathbb{R} \); the radial quantum number \( n \), which is \( n = 0, 1, 2, \ldots \) for bound states and \( n \in \mathbb{R} \) for unbound states; the orbital quantum number \( l = 0, 1, 2, \ldots \) and the azimuthal quantum number \( m = -l, -l+1, \ldots, -1, 0, 1, \ldots, 1, l \).

Now we need to define the statistical weights of the energy levels (15). We assume that the considered system of \( N \) particles is immersed into thermostat with temperature \( T \). To find the weights \( p_\alpha \) in (12) we can proceed as follows. Define the entropy
\[ S = - \sum_\alpha p_\alpha \ln p_\alpha. \]
The weights \( p_\alpha \) have to satisfy the normalization condition in (11) and give an average energy per particle according to (12), that is
\[ \sum_\alpha p_\alpha = 1, \quad \frac{1}{N}\langle H_N \rangle = \sum_\alpha p_\alpha E_\alpha. \]

In addition, there can exist some constraints or selection rules which usually can be related to operators \( \hat{I} \) being integrals of motion whose averages can be written as
\[ \langle \hat{I} \rangle = \sum_\alpha p_\alpha I_\alpha. \]
For instance, \( \hat{I} \) can be a projector to a space of a given symmetry. Introduce the notation
\[ \pi_\alpha \equiv \exp(-\gamma I_\alpha), \]
where \( \gamma \) is a Lagrange multiplier. Minimizing the conditional entropy
\[ \tilde{S} = S + \beta \left( \frac{1}{N}\langle H_N \rangle - \sum_\alpha p_\alpha E_\alpha \right) + \]
\[ + (1 - \ln Z) \left( \sum_\alpha p_\alpha - 1 \right) + \gamma \left( \langle \hat{I} \rangle - \sum_\alpha p_\alpha I_\alpha \right), \tag{16} \]
with the Lagrange multipliers $\beta = T^{-1}, \gamma$, and $1 - \ln Z$, we get
\[ p_\alpha = \frac{\pi_\alpha}{Z} \exp(-\beta E_\alpha); \quad Z = \sum_\alpha \pi_\alpha \exp(-\beta E_\alpha). \tag{17} \]

As an example of selection rules defining $\pi_\alpha$ consider the case when the second–order density matrix possesses the symmetry property
\[ \rho_2(\vec{r}_2, \vec{r}_1, \vec{r}_1', \vec{r}_2') = \pm \rho_2(\vec{r}_1, \vec{r}_2, \vec{r}_1', \vec{r}_2'). \]

Respectively, the functions $\Psi_\alpha$ in the expansion (7) are either symmetric or antisymmetric with respect to coordinate permutation,
\[ \Psi_\alpha(\vec{r}_2, \vec{r}_1) = \pm \Psi_\alpha(\vec{r}_1, \vec{r}_2). \]

The permutation $\vec{r}_1 \leftrightarrow \vec{r}_2$ is equivalent to the transformation
\[ \vec{r} \rightarrow -\vec{r}, \quad \vartheta \rightarrow \pi - \vartheta, \quad \varphi \rightarrow \varphi + \pi. \]

Using the property of spherical functions
\[ Y_{lm}(\pi - \vartheta, \varphi + \pi) = (-1)^l Y_{lm}(\vartheta, \varphi), \]
we have
\[ \Psi_\alpha(\vec{r}_2, \vec{r}_1) = (-1)^l \Psi_\alpha(\vec{r}_1, \vec{r}_2). \]

Therefore the coefficients $B_{\alpha\beta}$ in (7) should have the form
\[ B_{\alpha\beta} = \pi_\alpha^+ \pi_\beta^+ C_{\alpha\beta}, \]

in which
\[ \pi_\alpha^+ = \pi_l^+ \begin{cases} 1; & l = 0, 2, 4 \ldots \\ 0; & l = 1, 3, 5, \ldots \end{cases} \]
\[ \pi_\alpha^- = \pi_l^- \begin{cases} 0; & l = 0, 2, 4 \ldots \\ 1; & l = 1, 3, 5, \ldots \end{cases} \]

In this case, $\pi_\alpha^\pm$ is a projector to even or odd states, respectively. Then, from (17) we derive
\[ p_{nl} \equiv \sum_{Q,m} p_{Qnlm} = \pi_l^\pm \frac{2l+1}{Z_{int}} \exp \left\{ -\frac{\beta}{2} E_{nl}(N) \right\}; \]
\[ Z_{int} \equiv \sum_{nl} \pi_l^\pm (2l+1) \exp \left\{ -\frac{\beta}{2} E_{nl}(N) \right\}. \tag{18} \]

In this way, the average energy (12) takes the form
\[ \langle H_N \rangle = \frac{3}{2} NT + E(N), \tag{19} \]

where
\[ E(N) \equiv \frac{N}{2} \sum_{nl} p_{nl} E_{nl}(N). \tag{20} \]

The interpretation of the obtained result is straightforward. Since we are thinking of the considered system as of an $N$–particle cluster, we may say that the first term in (19) is the kinetic energy of the cluster, and (20) is the internal energy of particles inside the cluster. A part of the spectrum $E_{nl}(N)$ must correspond to bound states. In order that we could, in principle, speak about an $N$–particle cluster, the number of bound states must be not less than $N$. 


To be able to form bound states, the particles should interact with each other through forces containing an attractive part. The interaction potential in the reduced Hamiltonian (3) includes the factor \((N - 1)\). When \(N \gg 1\), then, even if the potential \(\Phi\) is small, the product \((N - 1)\Phi\) can be large. Moreover, the interaction between particles forming bound states is practically never small. All this means that the standard perturbation theory will not work for describing bound states. However, the problem is treatable by the controlled perturbation theory \([55-58]\) which is applicable to arbitrary strong interactions.

For demonstrational purpose, let us take an attractive potential of power law

\[
\Phi(r) = -Ar^{-\nu},
\]

in which \(A, \nu > 0\) and \(r \in \mathbb{R}_+\). Then the Hamiltonian (14) reads

\[
H_N(r) = -\frac{1}{2\mu} \frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} - (N - 1) \frac{A}{r^\nu}.
\]

The latter, using a scaling, can be reduced to the dimensionless form

\[
H = -\frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} - g r^{-\nu}.
\]

The return from (23) to (22) is made by substituting

\[
H \rightarrow \frac{H_N(r)}{\omega}; \quad \omega \equiv \left(\mu^\nu A^2\right)^{1/(2-\nu)},
\]

\[r \rightarrow \sqrt{\mu\omega} r, \quad g \rightarrow N - 1.\]

As zero approximation we may accept the Hamiltonian

\[
H_0 = -\frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} - \frac{u}{r}
\]

with the Coulomb interaction including yet unknown parameter \(u\). The eigenfunctions of (25) are

\[
\chi_{nl}^{(0)}(r) = \left[\frac{n!u}{(n+2l+1)!}\right]^{1/2} \frac{1}{n+l+1}\left(\frac{2ur}{n+l+1}\right)^{l+1} \times
\]

\[\times \exp\left(-\frac{ur}{n+l+1}\right) L_n^{2l+1} \left(\frac{2ur}{n+l+1}\right),\]

where \(L_n^l\) is an associate Laguerre polynomial. The eigenvalues of (25) are

\[
E_0(n,l,g,u) = -\frac{u^2}{2(n+l+1)^2}.
\]

Starting from (25), we can invoke the Rayleigh–Schrödinger perturbation theory with the perturbation

\[
\Delta H = \frac{u}{r} - \frac{g}{r^\nu}.
\]

In doing this, we encounter the integral

\[
J_n^l(\nu) \equiv \int_0^\infty t^{2l+2+\nu} e^{-t} L_n^{2l+1}(t) L_s^{2l+1}(t) dt.
\]

The latter can be presented as a sum. For instance, if \(s = n\), then

\[
J_n^l(\nu) = \frac{(n+2l+1)!}{n!} \sum_{p=0}^n \frac{(-1)^p \Gamma(p+2l+3+\nu)}{p!(n-p)!\Gamma(p+2l+2)} \varphi_n(-p-1-\nu),
\]
where
\[ \varphi_n(x) \equiv \frac{\Gamma(n+x)}{\Gamma(x)}; \quad \varphi_0(x) \equiv 1. \]

In particular,
\[ J_{nn}'(-1) = \frac{(n + 2l + 1)!}{n!}, \quad J_{00}'(-\nu) = \Gamma(2l + 3 - \nu). \]

For the first approximation we have
\[ E_{1}(n, l, g, u) = E_{0}(n, l, g, u) + \frac{u^2}{(n + l + 1)^2} - \frac{g u^\nu}{(n + l + 1)^2} A_{nl}(\nu); \tag{28} \]
here
\[ A_{nl} = \frac{n! J_{nn}'(-\nu)}{(n + 2l + 1)!} \left( \frac{2}{n + l + 1} \right)^{\nu - 1}, \]
\[ A_{0l} = \frac{\Gamma(2l + 3 - \nu)}{(2l + 1)!} \left( \frac{2}{l + 1} \right)^{\nu - 1}. \]

The procedure can be continued yielding \( E_k(n, l, g, u) \). Then, at each step \( k \), the unknown parameter \( u \) is to be transformed to a function \( u_k(n, l, g) \), such that the sequence \( \{e_k(n, l, g)\}_{k=0}^\infty \) of terms
\[ e_k(n, l, g) = E_k(n, l, g, u_k(n, l, g)) \tag{29} \]
would be convergent. Because of their role of forcing the convergence of the approximation sequence, the functions \( u_k(n, l, g) \) are called control, or governing, functions. Their explicit form is defined by fixed–point conditions. One of the simplest such conditions is the condition of minimal sensitivity \[59]\)
\[ \frac{\partial}{\partial u_k} E_k(n, l, g, u_k) = 0. \tag{30} \]

When equation (30) has no solution for the control function \( u_k \), one can use other types of fixed–point conditions \[55-58\]. If there exist several solutions for \( u_k \), than one has to resort to the stability analysis \[57,60\] choosing that solution which makes the procedure more stable.

In the first approximation we have only one solution for the control function
\[ u_1(n, l, g) = [\nu A_{nl}(\nu) g]^{1/(2-\nu)}. \tag{31} \]
From (28) and (29) we find
\[ e_1(n, l, g) = -\frac{(2 - \nu) u_1^2(n, l, g)}{2n(n + l + 1)^2}. \tag{32} \]
Eq.(32) shows that for \( \nu \geq 2 \) there are no bound states since all energy levels become positive moving to the continuous spectrum. When \( \nu = 1 \), then
\[ u_1(n, l, g) = g, \quad A_{nl}(1) = 1 \quad (\nu = 1), \]
and (32) yields
\[ e_1(n, l, g) = -\frac{g^2}{2(n + l + 1)^2} \quad (\nu = 1), \]
that is, we get an exact spectrum corresponding to the Coulomb potential.

For asymptotically small powers \( \nu \to 0 \), since
\[ J_{nn}'(0) = 2(n + l + 1) \frac{(n + 2l + 1)!}{n!}, \quad A_{nl}(0) = (n + l + 1)^2, \]
from (31) we have
\[ u_1(n, l, g) \simeq (n + l + 1)\sqrt{g\nu} \quad (\nu \to 0). \]

Therefore (32) gives
\[ \lim_{\nu \to 0} e_1(n, l, g) = -g. \]

In the case of \( n = 0 \), (32) becomes
\[ e_1(0, l, g) = -2 - \frac{\nu}{8\nu} \left[ 2\nu \Gamma(3 - \nu) g \right]^{2/2}, \quad (33) \]

And the ground–state energy level, when \( n = l = 0 \), is
\[ e_1(0, 0, g) = -2 - \frac{\nu}{8\nu} \left[ 2\nu \Gamma(3 - \nu) g \right]^{2/2}. \quad (34) \]

We calculated also the second–order approximation \( e_2(n, l, g) \) and the corrected first approximation, following the method of refs.[57,58,60]. The latter approximation has the form
\[ e_1^*(n, l, g) = e_1(n, l, g) \exp\{\lambda_1(n, l)\delta_*\}, \quad (35) \]
in which \( \lambda_1(n, l) \) is a local Lyapunov exponent for the approximation flow and \( \delta_* \) is a damping parameter. However, we shall limit ourselves by the first approximation (32) because the expressions for the second and for the corrected first approximations are essentially more cumbersome, although, as numerical analysis has shown, they do not differ much in accuracy from the first approximation.

The stability of the calculated procedure in the controlled perturbation theory [55-58,60] can be checked in the following way. Define the coupling function \( g_k(n, l, f) \) by the equation
\[ E_0(n, l, g, u_k(n, l, f)) = f. \quad (36) \]

This, in the case of (26) and (31), leads to the equality
\[ u_1(n, l, g) = (n + l + 1)\sqrt{-2f}. \]

For the coupling function we obtain
\[ g_1(n, l, f) = \frac{(n + l + 1)^{2-\nu}}{\nu A_{nl}(\nu)} (-2f)^{1-\nu/2}. \quad (37) \]

Now we have to define the points of the trajectory of the approximation cascade as
\[ y_k(n, l, f) = e_k(n, l, g_k(n, l, f)). \quad (38) \]

The starting point is \( y_0(n, l, f) = f \) and the first point is
\[ y_1(n, l, f) = \frac{2 - \nu}{\nu} f. \quad (39) \]

The mapping multipliers are
\[ \mu_k(n, l, f) = \frac{\partial}{\partial f} y_k(n, l, f), \quad (40) \]

so that
\[ \mu_1(n, l, f) = \frac{2 - \nu}{\nu}. \quad (41) \]

A necessary stability condition is
\[ |\mu_k(n, l, f)| < 1, \quad (42) \]
which shows the existence of contraction at the $k$-step with respect to the starting point. As we see, (41) satisfies (42) if $\nu > 1$.

Continuing the stability analysis for the second point of the cascade trajectory, we come to the mapping multiplier

$$
\mu_2(n, l, f) = \mu_1(n, l, f) + \lambda_1(n, l).
$$

(43)

Numerical calculations evince that the maximal Lyapunov exponent

$$
\lambda_1 \equiv \sup_{n, l} \lambda_1(n, l)
$$

(44)

is positive and small, $0 < \lambda_1 \ll 1$. Whence, the maximal mapping multiplier (43) is

$$
\sup_{n, l} |\mu_2(n, l, f)| = \left| \frac{2 - \nu}{\nu} + \lambda_1 \right|.
$$

The stability condition (42) for the mapping multiplier (43) is uniformly valid for all $n, l$ if

$$
\nu > \frac{2}{2 - \lambda_1} \simeq 1 + \frac{\lambda_1}{2}.
$$

(45)

Another stability condition requires that the Lyapunov exponents $\lambda_k$ would be negative [58,60].

To check the accuracy of the procedure, let us introduce the notation

$$
e_k(n, l) \equiv e_k(n, l, 1),
$$

(46)

using which (29) can be written as

$$
e_k(n, l, g) = e_k(n, l)g^{2/(2-\nu)}.
$$

(47)

The energy levels (46) can be compared with those obtained by direct numerical solution of the corresponding Schrödinger equation [61,62].

The Schrödinger equation with the Hamiltonian (23) can also be solved in the quasiclassical approximation [63] which yields

$$
e_{WB}(n, l, g) = \left\{ \sqrt{\frac{2}{\pi}} \frac{2 - \nu}{2 - \nu} \frac{2n + l + 1 + (\nu - 1)(2l + 1)}{2n + l + 1} \times \right.$$

$$
\left. \times \Gamma \left( \frac{2 - \nu}{2\nu} \right) / \Gamma \left( \frac{1}{\nu} \right)^{2\nu/(2-\nu)} g^{2/(2-\nu)} \right\} \frac{2 - \nu}{2 - \nu}.
$$

(48)

There exists a generalization of the quasiclassical approximation based on the use of modified Airy functions [64], but this technique, as it seems, is useful only for one-dimensional problems.

Introducing the notation

$$
e_{WB}(n, l) \equiv e_{WB}(n, l, 1),
$$

(49)

we can cast (48) into

$$
e_{WB}(n, l, g) = e_{WB}(n, l)g^{2/(2-\nu)}.
$$

(50)

The form (49) is convenient to compare with direct numerical solutions [61,62].

The most proper characteristic of the precision of an approximate method is, apparently, the relative error. Thus, the error of (46) is defined as a percentage deviation

$$
\varepsilon_k(n, l) \equiv \frac{e_k(n, l) - e(n, l)}{|e(n, l)|} \cdot 100\%.
$$

from an exact numerical value $e(n, l)$. The percentage errors of (35) and (48) are defined in the same way, as $\varepsilon_k(n, l)$ and $\varepsilon_{WB}(n, l)$, respectively. The uniform accuracy of an approximation, with respect to all energy levels, is characterized by the maximal error

$$
\varepsilon_k \equiv \sup_{n, l} |\varepsilon_k(n, l)|.
$$
Analogously, the maximal errors $\varepsilon_1^*$ and $\varepsilon_{WKB}$ are defined.

The accuracy of the controlled perturbation theory and that of the quasiclassical approximation, for power–law potentials, is demonstrated in tables I–III, as compared to the exact numerical values $e(n,l)$ and with each other. In the table I the results are presented for the potential (21) with the power $\nu = 0.2$. The maximal errors are $\varepsilon_1 = 0.8\%$ and $\varepsilon_{WKB} = 4\%$. The errors for the second approximation $e_2(n,l)$ and for the corrected first approximation $e_1^*(n,l)$ are not displayed since they are very close to $e_1(n,l)$. The accuracy of (35) in the case of the damping parameter $\delta_* = 1$ is practically the same as in the case of $\delta_* = 1/2$, for the latter case being slightly better. The accuracy, when passing from $e_1(n,l)$ to $e_2(n,l)$, does not improve because for $\nu = 0.2$ the stability condition (45) is not valid. The corrected approximation $e_1^*(n,l)$ is not more accurate than $e_1(n,l)$ since the Lyapunov exponent (44) is positive.

Table II presents the calculations for $\nu = 0.8$. The maximal errors are $\varepsilon_1 = 0.3\%$ and $\varepsilon_{WKB} = 6\%$. The accuracy of $e_2$ and $e_1^*$ is pretty much the same as of $e_1$. The maximal error $\varepsilon_1^*$ practically does not change when replacing $\delta_* = 1$ by $\delta_* = 1/2$. The absence of the improvement in accuracy is again caused by the fact that the stability conditions do not hold for $\nu = 0.8$. Nevertheless, as in the previous case of $\nu = 0.2$, the controlled perturbation theory is much more accurate than the quasiclassical approximation.

Table III contains the results for $\nu \geq 1$. For $\nu = 1$, all approximations become exact answers. For $\nu > 1$ the stability condition (45) now holds, and the accuracy of $e_2$ is slightly higher than of $e_1$. The Lyapunov exponent (44), as earlier, is positive, so $e_1^*$ does not improve $e_1$. Again, the quasiclassical approximation is essentially less precise than the controlled perturbation theory.

IV. EVAPORATION TEMPERATURE

For the considered case of the power–law attraction (21), the spectrum of the relative motion of particles inside a cluster, defined by eq.(13), has the form

$$E_{nl}(N) = \omega e(n,l)g^{2/(2-\nu)}, \quad (n = l = 0).$$

(51)

where

$$\omega = (\mu^* A^2)1/(2-\nu), \quad \mu = \frac{m_0}{2}, \quad g = N - 1.$$ 

The value of $e(n,l)$, as is shown in the previous section, can be calculated, with a good accuracy, by the controlled perturbation theory [55-58]. For example, we can use $e_1(n,l)$ from (32).

Define the ground–state level of (51) as

$$E_0(N) = E_{00}(N) \quad (n = l = 0).$$

(52)

Here we should substitute

$$e_1(0,0) = -\frac{2-\nu}{8\nu} [2\nu \Gamma(3-\nu)]^{2/(2-\nu)}.$$ 

(53)

The internal energy of particles inside a cluster is given by (20) with the spectral weights (18). The whole spectrum has two parts, discrete and continuous. The discrete spectrum corresponds to bound states with negative energies (51). The continuous spectrum is related to unbound states with positive energies.

When temperature increases from zero, the internal energy of a cluster (20) increases from a negative value to zero and then to positive values. The characteristic temperature, $T_c$, at which the cluster ceases to exist, can be defined as the temperature where $E(N)$ becomes zero,

$$E(N) = 0 \quad (T = T_c).$$

This temperature may be named the evaporation temperature. The absolute value $|E(N)|$ is called the binding energy. So, the evaporation temperature is that where the binding energy is zero.

Approximately, the evaporation temperature can be obtained as follows. Note that when the temperature of thermostat is such that $2T \ll |E_0(N)|$, then the lower bound states are mainly occupied, while the unbound states of continuous spectrum are practically empty. This situation describes a well defined cluster. Recall that the thermostat here models surrounding matter, and temperature can be interpreted as a measure for the kinetic energy of collisions. If the latter are intensive, so that $2T \gg |E_0(N)|$, then the bound states are strongly depleted and the
unbound states are essentially populated. This means that the cluster itself is actually destroyed, since a cluster is well defined only if the particles are bound inside it. The characteristic temperature

\[ T_c(N) = \frac{1}{\omega} |E_0(N)| \]  

(54)
specifying the desintegration of a cluster can be called the evaporation temperature, or the condensation temperature if the inverse process of lowering temperature is considered. The energy \( E_0(N) \) in (54), defined in (52), is the ground-state energy of a pair of particles from the collection of \( N \) particles. This explains the appearance of the factor \( \frac{1}{2} \) in (54).

It is convenient to introduce the dimensionless evaporation temperature

\[ t_c(N) \equiv \frac{T_c(N)}{\omega}. \]  

(55)

For the latter, taking account of (51) and (53), we have

\[ t_c(N) = \frac{2 - \nu}{16\nu} |2\nu\Gamma(3 - \nu)(N - 1)|^{2/(2 - \nu)}. \]  

(56)

In the case of the purely Coulomb interaction \( \nu = 1 \), (56) reduces to the expression

\[ t_c(N) = \frac{1}{4} (N - 1)^2 \quad (\nu = 1). \]

Then (54) is recovered by multiplying the latter by \( \omega \) with

\[ \omega = \frac{\alpha^2}{2m_0c^2}; \quad \alpha \equiv \frac{A}{\hbar c} \quad (\nu = 1). \]

if \( A = e^2 \), where \( e \) is the electron charge, then \( \alpha = 1/137 \) is the fine-structure constant. In the latter case, \( \omega = 13.613eV \), or \( 15.796 \times 10^4K \).

The evaporation of a cluster is the manifestation of its instability against excitations caused by the influence of surrounding. There can exist another instability limiting the size of a cluster. This is related to the definition of the cluster mass

\[ M_N \equiv m_0N + \frac{E(N)}{c^2} \geq 0 \]  

(57)
as of a nonnegative quantity. Here \( E(N) \) is the internal energy of particles inside the cluster, being given by (20). Due to the dependence of \( E(N) \) on temperature, the mass (57) is also dependent on \( T \), so that \( M_N \) increases together with \( T \). Let us introduce a function \( \gamma(T) \) by the relation

\[ E(N) = \frac{N}{2} \gamma(T)E_0(N), \]  

(58)
in which

\[ E_0(N) = \omega e(0,0)(N - 1)^{2/(2 - \nu)}. \]

At zero temperature, \( 0 < \gamma(0) \leq 1 \). With the notation (58) the cluster mass (57) reads

\[ M_N = m_0N + \frac{\omega\gamma(T)e(0,0)(N - 1)^{2/(2 - \nu)}}{2c^2}. \]  

(59)

As far as for \( T < T_c \) the function \( \gamma(T) \) is positive, and \( e(0,0) \) is always negative, the second term in (59) is negative. Therefore, with increasing \( N \), the cluster mass (59) decreases and becomes zero at \( N = N_0(T) \) which is

\[ N_0(T) = 1 + \left[ \omega \frac{2m_0c^2}{\gamma(T)e(0,0)} \right]^{1-\nu/2}. \]  

(60)

In the case of \( \nu = 1 \), since \( e(0,0) = -1/2 \), we have

\[ N_0(T) = 1 + \sqrt{\frac{8}{\alpha^2\gamma(T)}} \quad (\nu = 1). \]
If we assume that $\alpha = 1/137$ and take $\gamma(T) \approx 1/2$, then $N_0 \approx 549$.

Eq.(60) defines the maximal number of particles in a cluster. If $N$ surpasses $N_0$, the cluster desintegrates into several smaller clusters. With temperature increasing from zero to $T_c$, the maximal number of particles (60) increases. When $T \rightarrow T_c - 0$, then $\gamma(T) \rightarrow 0$. If we suppose that $\gamma(T) \sim T - T_c$ as $T \rightarrow T_c$, then $N_0(T) \sim (T - T_c)^{1-\nu/2}$. That is, the maximal number of particles in a cluster tends to infinity with the critical index $1 - \nu/2$. The function $\gamma(T)$ plays here the role of an order parameter.

The evaporation of a cluster, though reminds a phase transition, is, of course, not the same. Generally, we can consider a cluster of any number of particles $N > 1$. Even we may take $N = 2$. It would be too bold to speak about a phase transition for two particles. An actual evaporation–condensation phase transition occurs in an ensemble of many clusters, or droplets, which interact with surrounding as well as with each other. However, if the number of particles forming a cluster is very large, say $N \rightarrow \infty$, then the evaporation of such a cluster can have many features of a phase transition. For example, a crystal can be treated as a cluster. The transition of the particles of this cluster from bound to unbound states happens at the melting temperature $T_m$ which is an analog of the evaporation temperature. The temperature $T_m$ can be estimated as follows [65]. According to the meaning of the transition from bound to unbound states, the related characteristic temperature is to be close to the ground–state binding energy, $T_m \approx |E_0|$. The latter is about the effective depth of the interaction potential $|E_0| \approx \Phi_m$. So,

$$T_m = C \Phi_m,$$

where $C$ is a constant of the order of one. Take, e.g., the elements of the inert group interacting through the $12 - 6$ Lennard–Jones potential. Then $\Phi_m = \varepsilon$, where $\varepsilon$ is a constant of the Lennard–Jones potential. Estimates give $C = 1/\sqrt{2}$. The formula

$$T_m = \frac{\varepsilon}{\sqrt{2}}$$

evaluates the melting temperatures surprisingly well, which is demonstrated in table IV for $Ne$, $Ar$, $Kr$ and $Xe$ at zero pressure: The calculated $T_m$ is very close to the experimental value $T_m^{exp}$.

V. CONCLUSION

A cluster is defined as an object by $N$ particles in bound states. For any, arbitrary strong, interactions between particles the spectrum of bound states can be calculated with a good accuracy by means of the controlled perturbation theory. The latter is about an order more accurate than the quasiclassical approximation.

The properties of a cluster in the vaccuum and inside matter can be essentially different. The differences are traced by analysing a simple model when surrounding matter is replaced by thermostat. With increasing temperature, the cluster begins to evaporate. At the characteristic temperature of evaporation, $T_c$, the cluster desintegrates into its constituents. The evaporation temperature is approximately equal to one half of the ground–state binding energy.

The number of particles in a cluster is limited by $N_0$ depending on the interaction potential between particles and the thermostat temperature. The limit $N_0$ increases with temperature, tending to infinity as $T \rightarrow T_c$.

The term evaporation is applicable to clusters of any number of particles $N > 1$. The evaporation of small clusters is rather a continuous process than an abrupt transformation. The evaporation of large clusters can acquire features of phase transitions.

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Table Captions

**Table I.** The accuracy of the energy levels calculated using the controlled perturbation theory and the quasiclassical approximation, for the interaction potential with $\nu = 0.2$.

**Table II.** The same as in table I, but for the potential with the power $\nu = 0.8$.

**Table III.** The accuracy of the ground–state energy found by using the controlled perturbation theory and the quasiclassical approximation, for potentials with different powers.

**Table IV.** The estimation of the melting temperature at zero pressure, for the inert–group crystals with the Lennard–Jones interaction.
Table I

| n | l  | \(\epsilon(n,l)\) | \(\epsilon_1(\%)\) | \(\epsilon_{WKB}(\%)\) | \(\epsilon_{WKB}/\epsilon_1\) |
|---|---|----------------|----------------|----------------|----------------|
| 0 | 0 | 0.72526 | 0.50 | -1.2 | 2.4 |
| 1 | -0.63319 | 0.29 | -2.8 | 9.7 |
| 2 | -0.58215 | 0.19 | -3.5 | 18 |
| 0 | 0 | -0.60834 | -0.32 | -0.40 | 1.3 |
| 1 | -0.56730 | 0.19 | -1.3 | 6.8 |
| 2 | -0.53733 | 0.24 | -2.0 | 8.3 |
| 0 | 0 | -0.55191 | -0.76 | -0.22 | 0.29 |
| 1 | -0.52680 | -0.04 | -0.83 | 21 |
| 2 | -0.50628 | 0.14 | -1.4 | 10 |

Table II

| n | l  | \(\epsilon(n,l)\) | \(\epsilon_1(\%)\) | \(\epsilon_{WKB}(\%)\) | \(\epsilon_{WKB}/\epsilon_1\) |
|---|---|----------------|----------------|----------------|----------------|
| 0 | 0 | -0.48336 | 0.21 | -2.0 | 9.5 |
| 1 | -0.19843 | 0.05 | -4.9 | 98 |
| 2 | -0.11707 | 0.20 | -5.8 | 29 |
| 0 | 0 | -0.18334 | -0.10 | -0.58 | 5.8 |
| 1 | -0.11151 | 0.29 | -2.2 | 7.6 |
| 2 | -0.07739 | 0.21 | -3.5 | 17 |
| 0 | 0 | -0.10517 | -0.27 | -0.18 | 0.67 |
| 1 | -0.07421 | -0.08 | -1.5 | 19 |
| 2 | -0.05635 | 0.17 | -2.3 | 14 |

Table III

| \(\nu\) | \(\epsilon(0,0)\) | \(\epsilon_1(\%)\) | \(\epsilon_2(\%)\) | \(\epsilon_{WKB}(\%)\) | \(\epsilon_{WKB}/\epsilon_2\) |
|-----|----------------|----------------|----------------|----------------|----------------|
| 1   | -0.5         | 0             | 0             | 0             | 1             |
| 1.25| -0.69938     | 1.4           | 1.2           | 7.1           | 5.9           |
| 1.5 | -2.3687      | 12            | 11            | 28            | 2.5           |

Table IV

| \(\epsilon(K)\) | \(T_m = \frac{\epsilon^2}{\sqrt{2}}(K)\) | \(T_{mexp}(K)\) |
|----------------|-----------------------------------|----------------|
| Ne            | 36                                | 25             |
| Ar            | 121                               | 86             |
| Kr            | 163                               | 115            |
| Xe            | 232                               | 163            |