Particle finite-size effects as a mean-field approximation

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It is shown that the equation of state of a classical Boltzmann gas with two-particle interactions can be written without any approximations in a one-particle representation or in terms of a phenomenological mean-field model. The use of this model makes it possible to formulate a thermodynamically consistent scheme for taking the finite size of the particles of the medium into account. The possibility of the appearance of intermediate statistics in the appropriate approach is pointed out.

1. THE EXTENDED PHENOMENOLOGICAL MEAN-FIELD MODEL

The problem of taking the finite volume of the particles of a medium into account has recently been actively discussed in connection with investigations of the equation of state (ES) of nuclear matter,[1] the determination of which is one of the principal goals of heavy-ion physics. Explicit allowance for the hard core of the nucleons or for their intrinsic volume is necessary to describe the high-density nuclear matter that is formed when nuclei collide. At the same time, at low baryon-number densities and high temperatures serious problems arise if we regard hadronic matter as a system of point particles (for more detail, see Refs. 2 and 3).

Approaches to taking excluded-volume effects into account have been proposed in a number of papers.[4-7] The authors set themselves the goal of modeling the behavior of the basic thermodynamic quantities when the particles have finite sizes. In those papers this goal is achieved at the expense of violation of the thermodynamic consistency of the quantities, and, therefore, from the point of view of statistical thermodynamics, such approaches may be regarded as preliminary.

In the present paper we propose a scheme for taking the intrinsic size of the particles of a medium (nucleons) into account, based on the use of a relationship between the one-particle spectrum (one-particle potential) and the excess pressure incorporating information about the collisionality of the gas. The one-particle spectrum, established in the Boltzmann region, is then used in the quantum region too, in a phenomenological mean-field model involving no violation of thermodynamic consistency. We recall briefly the basic relations of this model.

The mean-field model (MFM) is a rather popular theoretical method for studying the ES of nuclear matter.[8-11] In this model it is assumed that in the system there is a certain mean (molecular) field $U(n, T)$ (n is the density of the particles and T is the temperature) that reflects the interaction between the particles. The appearance in the system of a new thermodynamic degree of freedom (the mean field) leads to the appearance of an excess pressure $P(n, T)$. Consequently, if there are no other types of interaction in the system besides those which are described by the one-particle potential $U(n, T)$, the expression for the pressure has the following form:

$$p(T,\mu)=\frac{gT}{a}\int\frac{d^3k}{(2\pi)^3}\ln\Big[1+a\times\exp\Big(-\frac{e_0(k)+U(n,T)-\mu}{T}\Big)\Big]+P(n,T), \qquad (1)$$

where μ is the chemical potential, g is the degeneracy factor, $n = n(T, \mu)$, $a = \pm 1$ (the upper sign corresponds to Fermi–Dirac statistics and the lower sign to Bose–Einstein statistics), and $e_0(k) = \mathbf{k}^2/2m$ in the nonrelativistic case while $e_0(k) = (m^2 + \mathbf{k}^2)^{1/2}$ in the relativistic case (we adopt a system of units with $\hbar = k_B = 1$). The particle-number density is expressed in the standard way in terms of the one-particle distribution function

$$n(T,\mu)=g\int\frac{d^3k}{(2\pi)^3}f(k), \qquad (2)$$

where

$$f(k)=\Big[\exp\Big(\frac{e_0(k)+U(n,T)-\mu}{T}\Big)+a\Big]^{-1} \qquad (3)$$

is the distribution function, in which, for each fixed point in the (T, μ) plane, the free-particle spectrum has been shifted uniformly.

In order that the expressions (1) and (2) be thermodynamically consistent, i.e., that the formula $n = (\partial p/\partial\mu)_T$ be valid, it is necessary and sufficient that the following differential relation between the mean field and the excess pressure be fulfilled:[8,11]

$$n\frac{\partial U(n,T)}{\partial n}=\frac{\partial P(n,T)}{\partial n}. \qquad (4)$$

The latter is the analog of the well known relationship between the pressure and the chemical potential in the variables n and T:

$$n[\partial\mu(n,T)/\partial n]_T=[\partial p(n,T)/\partial n]_T.$$

The energy density, calculated using standard thermodynamic formulas, has the form

$$\varepsilon(T,\mu)=g\int\frac{d^3k}{(2\pi)^3}e_0(k)f(k)+nU(n,T)-P(n,T)+T\Big[\Big(\frac{\partial P(n,T)}{\partial T}\Big)_n-n\Big(\frac{\partial U(n,T)}{\partial T}\Big)_n\Big], \qquad (5)$$

whence it is easy to see that, if the mean field and excess pressure are linear functions of the temperature, the last four terms in (5) cancel each other and then, in a quantity such as the energy density, the interaction manifests itself only through the distribution function in the first integral term. As will be seen from the following, in the scheme proposed in the present paper this is a rather typical situation.

Given the definite expressions (1), (2), and (5) for the pressure, particle density, and energy density, we can find the entropy density from the Euler relation

$$\varepsilon+p=Ts+\mu n. \tag{6}$$

Note that in the phenomenological MFM the relation (2) is an equation for the particle density n for each point of the (μ, T) plane, solving which we can determine the remaining thermodynamic quantities. In addition, in contrast to self-consistent approaches, e.g., the Debye–Hückel method,[12] in the MFM formulation the mean field $U(n, T)$ is an external quantity and is specified using additional physical considerations. For example, very often in the construction of the ES of nuclear matter the mean field is chosen as a polynomial in the nucleon density, and the coefficients of this polynomial are determined from normalization to the properties of normal nuclear matter. Thus, it may be said that the MFM is formulated if the function $U(n, T)$ or $P(n,T)$ is specified.

To conclude this section, we note that in the present paper we have extended the concepts of the mean field and excess pressure slightly in comparison with those in the literature,[8,9,11] by including in these quantities a dependence on the temperature. As is easily seen, this generalization has not led to any fundamental changes in the formulation of the phenomenological MFM, which is contained in the relations (1)–(4), and only in derivative quantities such as the energy density and entropy density have new terms appeared (derivatives with respect to temperature). An argument in favor of the generalization made is the fact that only in the case of this extended dependence is the correspondence principle for the MFM fulfilled in general form, i.e., in the passage to the Boltzmann limit the MFM reduces to the well-known "exact" theory. We turn now to the proof of this assertion.

2. PHENOMENOLOGICAL MEAN-FIELD MODEL IN THE BOLTZMANN LIMIT

In this section we show that in the Boltzmann limit the phenomenological MFM formulated above is an "exact" thermodynamic theory of a gas with two-particle interaction. In fact, the partition function of the Boltzmann gas in the grand canonical ensemble has the form

$$\Xi(T,\mu,V)=\sum_{N=0}^{\infty}V^N g^N\int\frac{d^3k_1}{(2\pi)^3}\cdots\frac{d^3k_N}{(2\pi)^3}\times\exp\left[-\frac{1}{T}\left(\sum_{j=1}^{N}e_0(k_j)-\mu N\right)\right]\cdot\times\frac{1}{V^N N!}\int d^3r_1\ldots d^3r_N\exp\left[-\frac{U_{int}^{(N)}}{T}\right], \tag{7}$$

where

$$U_{int}^{(N)}=\sum_{i<j}^{N}\Phi(|\mathbf{r}_i-\mathbf{r}_j|) \tag{8}$$

is the pair-interaction energy of the system of N particles with two-particle interaction potential $\Phi(|\mathbf{r}|)$ and V is the volume of the system. When the conditions of the virial expansion are fulfilled this partition function can be represented in the following form:[13,14]

$$\ln\Xi=V\left(n+\sum_{i=2}^{\infty}B_i(T)n^i\right), \tag{9}$$

and, in addition, the relation

$$\ln\left[z_0\exp\left(\frac{\mu}{T}\right)\right]=\ln(n)+\sum_{i=2}^{\infty}\frac{i}{i-1}B_i(T)n^{i-1}, \tag{10}$$

is fulfilled, where $B_i(T)$ are the virial coefficients, e.g.,

$$B_2(T)=-\frac{1}{2}\int d^3r\left\{1-\exp\left[-\frac{\Phi(r)}{T}\right]\right\}$$

(for more detail, see Refs. 13 and 14), and z_0 is the one-particle partition function of the Boltzmann ideal gas:

$$z_0=g\int\frac{d^3k}{(2\pi)^3}\exp\left[-\frac{e_0(k)}{T}\right]. \tag{11}$$

We introduce the following notation:

$$P_B(n,T)=T\sum_{i=2}^{\infty}B_i(T)n^i, \tag{12}$$

$$U_B(n,T)=T\sum_{i=2}^{\infty}\frac{i}{i-1}B_i(T)n^{i-1}. \tag{13}$$

With this notation we can rewrite Eq. (10) in the form

$$n(T,\mu)=g\int\frac{d^3k}{(2\pi)^3}\exp\left[-\frac{e_0(k)+U_B(n,T)-\mu}{T}\right], \tag{14}$$

and, using $p=(T/V)\ln\Xi$, for the relation (9) we find the following form:

$$p(T,\mu)=Tn(T,\mu)+P_B(n,T). \tag{15}$$

As can be seen, the expressions (14) and (15) determining the thermodynamics of a Boltzmann gas of interacting particles have been obtained here without any approximations and can be regarded as the one-particle form of the original partition function (7). In addition, by direct inspection it is easy to establish that the functions $P_B(n,T)$ and $U_B(n,T)$ introduced in (12) and (13) satisfy the thermodynamic-consistency condition (4) obtained in the MFM. Consequently, these quantities can be regarded as the Boltzmann excess pressure and the "exact" Boltzmann mean field, and the relations (12) and (13) as their virial expansions.

The next basic step in establishing the correspondence between the MFM and the Boltzmann gas of interacting particles is to take the Boltzmann limit in (1)–(3), which is formally implemented by letting $a\to 0$. As a result, for the MFM we obtain

$$n(T,\mu)=g\int\frac{d^3k}{(2\pi)^3}\exp\left[-\frac{e_0(k)+U(n,T)-\mu}{T}\right], \tag{16}$$

$$p(T,\mu)=Tn(T,\mu)+P(n,T). \tag{17}$$

Comparison with the corresponding expressions (14) and (15) for the Boltzmann gas with two-particle interaction leads to the conclusion that, if the MFM does indeed give a correct description of the thermodynamics of the system in the Boltzmann regime, the following asymptotic relations should hold:

$$U(n,T)\underset{a\to 0}{\rightarrow}U_B(n,T),\quad P(n,T)\underset{a\to 0}{\rightarrow}P_B(n,T),\tag{18}$$

i.e., the mean field (one-particle potential) and excess pressure of the MFM have Boltzmann limits that are given, according to the virial expansions (13) and (12), in terms of the parameters of the two-particle potential $\Phi(r)$. In addition, the asymptotic relations (18) give sufficient grounds to assume that, in their general form, these quantities depend both on the particle density and on the temperature, inasmuch as their Boltzmann limits depend in the general case on the temperature.

The constructive element of the relations obtained is clarified if we formulate in these terms the inverse problem of statistical thermodynamics—the restoration of the one-particle spectrum (mean field) from the known ES. In fact, if the ES (15) of a Boltzmann gas of interacting particles is known, then, according to (4), which, as we have seen is fulfilled for the quantities (12) and (13), we can determine the mean field

$$U_B(n,T)=\int_0^n\frac{1}{n'}\frac{\partial P_B(n',T)}{\partial n'}dn',\tag{19}$$

in which it is entirely natural to take $U_B(n=0,T)=0$. With the function $U_B(n,T)$ found in this manner, the relation (14) is transformed into an equation for the particle density for each fixed pair (T,μ). Consequently, the solution of this equation is a function $n(T,\mu)$, knowledge of which makes it possible, according to (15), to find the pressure as a function $p(T,\mu)$ of the temperature and chemical potential, and also the energy density and entropy as functions of these variables. In other words, this scheme makes it possible to go from the (T,n) ensemble to the (T,μ) ensemble without explicit use of the Helmholtz free energy.

We shall consider a system in which the interaction between the particles is determined by a short-range two-particle potential $\Phi(r)$. Suppose that for such a system the ES in the Boltzmann regime is known. Then the mean field $U_B(n,T)$ can be found by the inverse technique of statistical thermodynamics. In addition, the mean field can be determined approximately [see (13)] if the two-particle potential $\Phi(r)$ is known explicitly. The principal assumption, important for the subsequent analysis, is as follows: For the class of short-range two-particle potentials (or for the short-range part of the potential) we can set

$$U(n,T)\approx U_B(n.T),\tag{20}$$

where $U(n,T)$ is the mean field used in the entire range of the variables n and T, including the quantum region. In essence, the approximation (20) is the assumption that, for the system under consideration, the manifestation of the interaction of the particles on the level of the mean field is the same in classical and quantum statistics.

The interactions that determine the intrinsic sizes of the particles, i.e., repulsive two-particle potentials with a hard core, can certainly be assigned to this class. It can then be assumed that, if the mean field $U_B(n,T)$ effectively realizes an interparticle repulsion such that the particles are not superposed in configuration space in the Boltzmann case, then in the case of quantum statistics too this mean field "works" in an analogous manner. In fact, despite the spatial overlap of the wave functions (packets) of the particles in the region of quantum statistics, the matrix element of the two-particle interaction potential is nonzero only in a spatial region close to contact between the particles, this being induced by the appropriate behavior of the potential $\Phi(r)$; i.e., as in the classical case, the particles begin to interact when they "touch" each other. These considerations can explain qualitatively why, in the case of a short-range two-particle potential, a formulation of the MFM is possible in which the interaction is described both with quantum statistics (the symmetry of the many-particle wave function) and classically (the properties of the matrix element of the interaction potential). It is clear that this approximation ceases to work only in the region of ultrahigh densities, similar to that for close packing of the particles of the system.

Thus, the proposed scheme is a way of closing the MFM equations (1)–(5). This approximation can be used in the case when the ES in the classical region is known. To describe a system consisting of particles of finite volume, such an equation could be, e.g., the van der Waals equation of state.

The second possibility of applying the proposed scheme arises when the two-particle potential is known, making it possible to calculate approximately the excess pressure and mean field from (12) and (13) with a degree of accuracy specified by the capabilities of the computer.

3. EXAMPLES OF THE CONSTRUCTION OF A MEAN-FIELD MODEL WITH ALLOWANCE FOR THE FINITE SIZE OF THE PARTICLES

Using the scheme proposed in the preceding section, we shall consider a few examples of the construction of a mean-field model in which the finite size of the particles is taken into account.

The most orthodox approach to the problem of taking the intrinsic size of the particles into account is the hard-sphere model (HSM). The Padé approximation constructed on the first six virial coefficients of the HSM gives the excess pressure in the form[15]

$$P(x,T)=T\frac{x^2}{v_0}\frac{u(x)}{d(x)},\tag{21}$$

where $x=v_0n$, $v_0=\frac{2}{3}\pi d_N^3$ is four times the volume of a particle with diameter d_N, $u(x)=1+b_1x+b_2x^2$, $d(x)=1-b_3x+b_4x^2$, and the coefficients b_i have the following values:

i	1	2	3	4
b_i	0,063507	0,017329	0,561493	0,081313

The expression for the mean field corresponding to the excess pressure (21) has the relatively cumbersome form

$$\frac{U(x,T)}{T}=x\left[c_1+\frac{u(x)}{d(x)}\right]+c_2\ln(d(x))$$
$$+2c_3c_4\{\operatorname{arctg}[c_4(2b_4x-b_3)]+\operatorname{arctg}(c_4b_3)\},\tag{22}$$

where $c_1=b_2/b_4$, $c_2=(b_1b_4+b_2b_3)/2b_4^2$, $c_3=1+(b_1b_3b_4+b_2b_3^2-2b_2b_4)/2b_4^2$, and $c_4=(4b_4-b_3^2)^{-1/2}$. Consequently, substitution of the mean field (22) and excess pressure (21) into (1)–(5) leads to a formulation of the MFM in which the particles are represented as hard spheres. Here the result is undoubtedly no more accurate than the original equation of state, defined by (21).

The next, historically important, example is the van der Waals equation of state

$$p=\frac{Tn}{1-v_N n}, \tag{23}$$

where v_N, as in the previous example, is four times the intrinsic volume of a particle. We shall not consider that part of the equation of state that is related to the attraction of the particles. From (23) we find the excess pressure

$$P_{vdw}(n,T)=Tn\frac{v_N n}{1-v_N n} \tag{24}$$

and the corresponding mean field

$$U_{vdw}(n,T)=T\frac{v_N n}{1-v_N n}-T\ln(1-v_N n). \tag{25}$$

Equation (14), i.e., the equation for the density of the particles in the (T,μ) ensemble, has the following appearance in this case:

$$N=y_{vdw}(n,T)\,Vz_0\exp(\mu/T), \tag{26}$$

where we have introduced the factor

$$y_{vdw}(n,T)=\exp(-U_{vdw}(n,T)/T),$$

which is determined by the mean field and can be interpreted as the factor by which the configuration volume is reduced because the particles of the system have finite sizes. It is easy to see that the function

$$y_{vdw}(n)=(1-v_N n)\exp\left[-\frac{v_N n}{1-v_N n}\right] \tag{27}$$

depends only on the particle density and varies from unity to zero as the argument varies from zero to the critical density $n_c=1/v_N$. The figure shows the graph of this dependence.

If we start from the physically natural point of view that the intrinsic sizes of the particles are a manifestation of the interaction between the particles (this is principally the short-range repulsive interaction), then, according to the general analysis of (7)–(15), a Boltzmann gas of particles possessing intrinsic volume can be described without loss of generality in terms of a mean field. Then it must be recognized that the equation (26) for the density of the particles has a universal form and that the different approaches to taking the intrinsic sizes of the particles into account can be classified using the volume-truncation function—the free-configuration-space factor $y(n,T)$.

As a third example of the free-volume factor, consider a linear dependence on the particle density:

$$y_l(n)=(1-v_N n). \tag{28}$$

This factor corresponds to a mean field

$$U_l(n,T)=-T\ln(1-v_N n). \tag{29}$$

In this linear case, Eq. (14) can be solved explicitly, and one can obtain expressions for the principal thermodynamic quantities in the Boltzmann regime:

$$n(T,\mu)=\frac{n_{id}(T,\mu)}{1+v_N n_{id}(T,\mu)}, \tag{30}$$

$$p(T,\mu)=(T/v_N)\ln[1+v_N n_{id}(T,\mu)], \tag{31}$$

$$\varepsilon(T,\mu)=\frac{\varepsilon_{id}(T,\mu)}{1+v_N n_{id}(T,\mu)}, \tag{32}$$

where $n_{\rm id}(T,\mu)$ and $\varepsilon_{\rm id}(T,\mu)$ are the particle density and energy density of the ideal Boltzmann gas. It is obvious that this model, like the two previous models, is thermodynamically consistent.

Thus, for the given examples we see that the approaches to the introduction of a finite particle volume can be classified using the appropriate configuration-space-truncation function $y(n)$. For comparison, plots of $y_{vdw}(n)$ (the solid lines) and $y_l(n)$ (the dashed lines) are shown in the figure for three values of the characteristic size of the nucleon: $d_N=0.6$, 0.8, and 1.0 fm ($v_N=\frac{2}{3}\pi d_N^3$; along the abscissa, the particle density is plotted in units of the normal nuclear density $n_0=0.16\ \mathrm{fm}^{-3}$. As can be seen, the van der Waals free-configuration-space factor (27) is a more severe truncation of the volume accessible to the particles of the system, this being explained by the presence of the additional exponential factor in (27) in comparison with (28).

We must mention the recent article of Rischke *et al.*,[3] which is devoted to the problem considered in this paper. The starting point of the approach proposed by the authors of Ref. 3 is a formulation of the partition function in which the intrinsic volume v_0 of the particles is included in the spirit of the van der Waals excluded volume. In the terminology of the present paper, we may say, conventionally, that the mean field is thereby rigidly fixed, i.e., the authors of Ref. 3 make an attempt to describe the entire range of effects associated with the interaction of the particles at short distances (interaction modeled by the finite volume of the particles) by means of a single external parameter. However, as we have seen above, even for one and the same value of the parameter v_0 the character of the behavior of the free-volume factor (Fig. 1) can vary greatly, and this, in its turn, gives

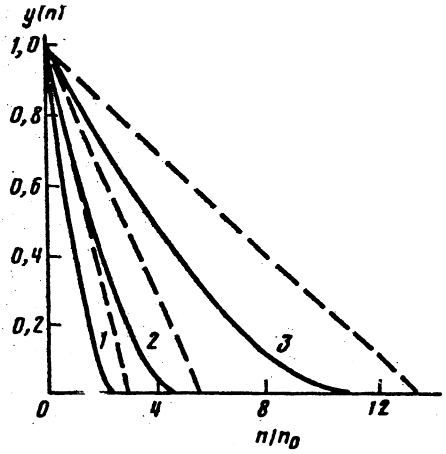

FIG. 1. Dependence of the free-volume factor on the particle density [the solid curves are $y_{vdw}(n)$, and the dashed curves are $y_l(n)$] for the following values of the characteristic nucleon size: $d_N=0.6$ fm (3); 0.8 fm (2); 1.0 fm (1) ($v_N=\frac{2}{3}\pi d_N^3$); here the particle density is in units of the normal nuclear density $n_0=0.16\ \mathrm{fm}^{-3}$. Each pair of curves crosses over the axis in the $n=1/v_N$.

rise to differing physical properties of the system. Consequently, it appears to us that, despite the attractiveness of the program proposed by the authors of Ref. 3, their approach has a limited range of application.

We wish to draw attention to one interesting phenomenon that can be explained using the approach described above. In the quantum-statistics region Eq. (2) can be rewritten as follows:

$$N=Vy(n)g\int\frac{d^3k}{(2\pi)^3}\left[\exp\left(\frac{e_0(k)-\mu}{T}\right)+ay(n)\right]^{-1}, \quad (33)$$

where $y(n)=\exp[-U(n,T)/T]$ is a certain free-volume-reduction factor for the system [e.g., $y(n)=1-v_N n$, and then $Vy(n)=V-v_N N$]. If in the statistical description of some system the configuration-volume decrease that arises on account of the finite volume of the particles is taken into account only in the form of the factor $Vy(n)$ multiplying the integral in (33), then it will be found, e.g., experimentally, that the system possesses intermediate statistics, since $0<y(n)<1$. But if we replace $y(n)$ under the integral by unity, the thermodynamic consistency will thereby be violated, and then, e.g., $n\neq(\partial p/\partial\mu)_T$. Consequently, in this approach the phenomenon of the onset of intermediate statistics is induced by the corresponding way of taking the intrinsic volume of the particles of the system into account. At the same time, as follows from the above account, the scheme for including the intrinsic volume of the particles as a mean field makes it possible to perform a thermodynamically consistent analysis in terms of the distribution function of an ideal gas with a uniformly shifted one-particle spectrum

4. CONCLUSION

To conclude, let us enumerate the results obtained.

1. In the case of Boltzmann statistics, the principal thermodynamic quantities of a gas with two-particle interaction admit a one-particle representation that coincides with the basic relations of the phenomenological mean-field model.

2. The mean field and excess pressure that are used in the MFM have Boltzmann limits. The latter quantities are the Boltzmann one-particle potential and the Boltzmann excess pressure, and can be found from the known classical equation of state [Eq. (19)] or calculated approximately [the relations (12) and (13)] for a known two-particle potential.

3. It is assumed that for short-range two-particle potentials the mean field as a function of the variables n and T is approximately the same for the Boltzmann region and the quantum region. Use of this approximation makes it possible to give in terms of the mean field a thermodynamically consistent description of a system consisting of particles of finite size (a two-particle repulsive potential with a hard core), and also to include in the description other forms of interactions.

According to the proposed scheme, to formulate a mean-field model describing a gas of particles of finite size one can take as the mean field (one-particle potential) $U(n, T)$ one of the functions obtained in Sec. 3 [see (22), (25), and (29)]. Substitution of this mean field into the distribution function (3) and subsequent solution of Eq. (2) give the dependence $n(T,\mu)$. The dependence $n(T,\mu)$ found makes it possible to determine finally the mean field $U[n(T,\mu),T]$ and the corresponding excess pressure $P[n(T,\mu),T]$ as functions of the temperature and chemical potential, and then also to find as functions of these variables: 1) the distribution function (3); 2) the pressure $p(T,\mu)$ (1); 3) the energy density $\varepsilon(T,\mu)$ (5); 4) the entropy density $s(T,\mu)$ (6).

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