Accounting for the Long-Range Forces in the Model of Hard Sphere

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A method for taking into account the long-range potential of atoms within the framework of the hard-sphere model is proposed. As shown, the thermodynamic quantities can be represented as a sum of three contributions—that of an ideal gas, the interaction of hard spheres, and the long-range potential. In the leading approximation on density, the corrections to the virial coefficient and heat capacity due to the smooth component of the potential are calculated. Attention is drawn to the fact that the effects determined by the long-range part of the potential can be described within the scope of the self-consistent field model.

Key words: gas, liquid, hard-sphere potential, long-range potential, virial coefficient, heat capacity, self-consistent field.

Запропоновано методу врахування далекосяжного потенціялу атомів у рамках моделі твердих сфер. Показано, що термодинамічні величини можна представити у вигляді суми трьох внесків — ідеального газу, взаємодії твердих сфер і далекосяжного потенціялу. В основному за густиною наближенні обчислено поправки до віріяльного коефіцієнта та тепломісткости для плавної складової потенціялу. Звернено увагу на те, що ефекти, які визначаються далекосяжною складовою потенціялу, можуть бути описані в рамках моделю самоузгодженого поля.

Ключові слова: газ, рідина, потенціял твердої сфери, далекосяжний потенціял, віріяльний коефіцієнт, тепломісткість, самоузгоджене поле.

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1. INTRODUCTION

In the theory of classical manyparticle systems, an important role is played by the model of hard spheres [1–5]. Although it is not possible to calculate the configuration integral even in the case of such a simple pair interaction potential, a sufficiently large number of virial coefficients are known here for low-density systems. The first four coefficients are known exactly, and higher order coefficients are calculated by numerical methods and the Monte Carlo method [1–5]. Within the framework of the hard-sphere model, there is also an exact solution of the Percus–Yevick integral equation for the pair correlation function [6, 7]. A significant drawback of the hard-sphere model is that the configuration integral and virial coefficients for it do not depend on temperature. In more realistic pair potentials, which depend only on the distance between particles, as a rule, it is possible to distinguish a region of strong repulsion at small distances and a rather smoothly varying part of the potential at large distances. The repulsive part usually differs little from the potential of hard spheres, so it is natural to model it by the potential of a hard sphere and, along with this, take into account the contribution to thermodynamic quantities of the long-range part of the potential.

In this work, based on such a decomposition of the pair potential, a method is proposed for calculating the thermodynamic characteristics of a gas and a liquid. It is shown that the free energy and thermodynamic quantities such as the pressure, entropy, heat capacity, chemical potential can be represented as a sum of three contributions—that of an ideal gas, the interaction of hard spheres, and the long-range potential. Corrections for the long-range part of the potential to thermodynamic quantities, in particular to the virial coefficient and heat capacity, are calculated in the leading approximation on density. It is noted that the self-consistent field model is applicable to describe the long-range interaction.

2. THERMODYNAMIC RELATION IN THE MODEL OF HARD SPHERES WITH ACCOUNT OF THE LONG-RANGE PART OF THE POTENTIAL

The free energy of a system of N particles $F = -T\ln Z_N$ is calculated through the partition function, which can be represented as

$$Z_N = \left(\frac{r_0}{\Lambda}\right)^{3N} \frac{Q_N}{N!}, \tag{1}$$

where

$$\Lambda \equiv \left(\frac{h^2}{2\pi m T}\right)^{1/2} \tag{2}$$

is the thermal de Broglie wavelength, h is the Planck's constant, T is the temperature, m is the mass of an atom. The configuration integral in (1) is defined by the formula

$$Q_N = \frac{1}{r_0^{3N}} \int e^{-\beta U(q)} dq, \tag{3}$$

where the designations are used: $q \equiv \{\mathbf{r}_1, \mathbf{r}_2,...,\mathbf{r}_N\}$, $dq \equiv d\mathbf{r}_1 d\mathbf{r}_2,...,d\mathbf{r}_N$ and $\beta = 1/T$. In formulas (1) and (3), a certain characteristic distance r_0 is introduced, which determines the conditional size of an atom. In what follows, this parameter will signify the radius of a hard sphere. The interaction between particles is realized through the pair potential, so that in (3)

$$U(q) \equiv \sum_{N \geq i > j \geq 1} U(r_{ij}), \tag{4}$$

where for brevity $r_{ij} \equiv |\mathbf{r}_i - \mathbf{r}_j|$. Then the exponent in (3) can be written in the form $e^{-\beta U(q)} = \prod_{N \geq i > j \geq 1} e^{-\beta U(r_{ij})}$. We choose the potential of the pairwise interaction of atoms as a sum of the potential of hard spheres $U_H(r_{ij})$ and the long-range part $U_L(r_{ij})$:

$$U(r_{ij}) \equiv U_H(r_{ij}) + U_L(r_{ij}), \tag{5}$$

where

$$U_H(r_{ij}) = \begin{cases} \infty, & r < r_0, \\ 0, & r > r_0. \end{cases} \tag{6}$$

The structure of the form (5) is inherent, for example, for the Sutherland potential

$$U(r_{ij}) = \begin{cases} \infty, & r_{ij} < r_0, \\ -\varepsilon \left(\dfrac{r_0}{r_{ij}}\right)^6, & r_{ij} > r_0. \end{cases} \tag{7}$$

A similar form is characteristic for other model potentials. There-

fore, for the modified Lennard–Jones potential, we have

$$U\left(r_{ij}\right) = \begin{cases} \infty, & r_{ij} < r_0, \\ 4\varepsilon\left[\left(\dfrac{r_0}{r_{ij}}\right)^{12} - \left(\dfrac{r_0}{r_{ij}}\right)^{6}\right], & r_{ij} > r_0. \end{cases} \tag{8}$$

The configuration integral of the model of hard spheres has the form

$$Q_N^{(H)} = \frac{1}{r_0^{3N}} \int \prod_{N \geq i > j \geq 1} \theta\left(\frac{r_{ij}}{r_0} - 1\right) dq \,, \tag{9}$$

where

$$\theta\left(x\right) = \begin{cases} 1, & x > 0, \\ 0, & x < 0, \end{cases} \tag{10}$$

is the stepwise function. With such decomposition, the full configuration integral can be represented as a sum

$$Q_N = Q_N^{(H)} + Q_N^{(L)} \,, \tag{11}$$

where

$$Q_N^{(L)} = \frac{1}{r_0^{3N}} \int \prod_{N \geq i > j \geq 1} \theta\left(\frac{r_{ij}}{r_0} - 1\right)\left[\prod_{N \geq k > r \geq 1} e^{-\beta U_L(r_{kr})} - 1\right] dq \,. \tag{12}$$

Thus, for potentials that have the form of a sum of the potential of hard spheres and the smooth long-range part, the configuration integral also has the form of a sum of contributions from the potential of hard spheres and the long-range part (11). It is convenient to introduce the "reduced" configuration integrals

$$\tilde{Q}_N^{(H)} \equiv \frac{Q_N^{(H)}}{Q_N^{(0)}} \,, \qquad \tilde{Q}_N^{(L)} \equiv \frac{Q_N^{(L)}}{Q_N^{(0)}} \,, \tag{13}$$

where $Q_N^{(0)} \equiv \left(V/r_0^3\right)^N$ is the configuration integral of an ideal gas. Then the free energy can be written as a sum of three contributions $F = F_0 + F_H + F_L$, where

$$F_0 = -NT\ln\left(\frac{e\upsilon}{\Lambda^3}\right) \tag{14}$$

is the free energy of an ideal gas, $\upsilon = V/N$ is the volume per one particle,

$$F_H = -T \ln \tilde{Q}_N^{(H)} \tag{15}$$

is the contribution from collisions of hard spheres, and

$$F_L = -T \ln\left(1 + \frac{\tilde{Q}_N^{(L)}}{\tilde{Q}_N^{(H)}}\right) \tag{16}$$

is the contribution from the long-range part of the interaction. Note that not only $\tilde{Q}^{(L)}$, but also the configuration integral of the model of hard spheres $\tilde{Q}_N^{(H)}$ enters into F_L. Other thermodynamic quantities can also be represented as a sum of three contributions. So far, no approximations have been made in deriving the formulas.

3. CALCULATION OF CORRECTIONS FOR THE LONG-RANGE PART OF THE POTENTIAL

In a sufficiently dilute system, it is possible to account for the interaction using the group expansion in powers of density [1–5]. For this purpose, the transition to Mayer functions

$$f_H\left(r_{ij}\right) = \theta\left(\frac{r_{ij}}{r_0} - 1\right) - 1, \qquad f_L\left(r_{ij}\right) = e^{-\beta U\left(r_{ij}\right)} - 1, \tag{17}$$

is employed. Taking into account the first correction for the dimensionless density $n\upsilon_a = \upsilon_a/\upsilon$, where $\upsilon_a = 4\pi r_0^3/3$ is the 'volume' of an atom, for the configuration integral of the model of hard spheres, we have

$$\tilde{Q}_N^{(H)} \approx 1 - \frac{N}{2}\frac{\upsilon_a}{\upsilon}. \tag{18}$$

Note that the use of the formula $\ln(1 + x) \approx x$ in calculating the free energy (15) is valid under the condition $N < \upsilon/\upsilon_a$ that is satisfied for a highly dilute gas [3].

In the leading approximation on density, the configuration integral for the long-range part of the potential is given by the formula

$$\tilde{Q}_N^{(L)} = \frac{N\left(N-1\right)}{2}\frac{4\pi}{V}\int\limits_{r_0}^{\infty} dr r^2 \left[e^{-\beta U_L(r)} - 1\right]. \tag{19}$$

Taking into account the main correction to formulas of the theory of an ideal gas in the ratio υ/υ_a, the full free energy takes the form

$$F = -NT \ln\left(\frac{\upsilon e}{\Lambda^3}\right) + \frac{NT}{2}\frac{\upsilon_a}{\upsilon} - \frac{3}{2}NT\frac{\upsilon_a}{\upsilon}J(T), \tag{20}$$

where

$$J(T) = \int\limits_1^\infty dx\, x^2 \left[e^{-\beta U_L(r_0 x)} - 1\right]. \tag{21}$$

Let us present formulas for the basic thermodynamic quantities in this approximation. The gas equation of state has the form

$$p = \frac{T}{\upsilon}\left(1 + \frac{B}{\upsilon}\right). \tag{22}$$

The virial coefficient B in the model of hard spheres is independent of temperature $B_H = \upsilon_a/2$. The calculation of the virial coefficient with account of the long-range part of the potential based on the formulas (16), (17), (21) gives

$$B(T) = B_H\left[1 - 3J(T)\right], \tag{23}$$

For example, for the Sutherland potential (7), the integral (21) has the form

$$J(T) = \int\limits_1^\infty dx\, x^2 \left[e^{\frac{\varepsilon}{T x^6}} - 1\right] = \frac{1}{6}\sqrt{\frac{\varepsilon}{T}}\int\limits_0^{\frac{\varepsilon}{T}} \frac{dy}{y^{3/2}}\left(e^y - 1\right). \tag{24}$$

Accounting for the long-range component of the potential leads to the fact that at low temperatures the virial coefficient becomes negative, changing sign at the Boyle temperature T_B, which is determined by the formula

$$J(T_B) = \frac{1}{3}. \tag{25}$$

In the case of the Sutherland potential $T_B = 1.17\varepsilon$.

For the entropy $S = -(\partial F/\partial T)_{V,N}$ in this approximation, we have

$$S = N\ln\left(\frac{\upsilon e^{5/2}}{\Lambda^3}\right) - \frac{N}{2}\frac{\upsilon_a}{\upsilon} + \frac{3N}{2}\frac{\upsilon_a}{\upsilon}\left(J + T\frac{dJ}{dT}\right). \tag{26}$$

Note that the contribution to the entropy from collisions of hard spheres does not depend on temperature, and the contribution to the temperature dependence of entropy comes only from the long-range interaction.

The energy $E = F + ST$ is determined by the formula

$$E = \frac{3}{2} NT \left(1 + \frac{\upsilon_a}{\upsilon} T \frac{dJ}{dT} \right).$$ (27)

Collisions of hard spheres also do not contribute to the total energy. Let us also give a formula for the chemical potential $\mu = -(\partial F/\partial N)_{T, V}$:

$$\mu = -T \ln \left(\frac{\upsilon}{\Lambda^3} \right) + T \frac{\upsilon_a}{\upsilon} - \frac{3}{2} T \frac{\upsilon_a}{\upsilon} J.$$ (28)

Since the contribution to the entropy of collisions of hard spheres does not depend on temperature, such collisions do not contribute to the heat capacity either. The contribution to the heat capacity is determined only by the long-range part of the interaction potential

$$C_V = \frac{3}{2} N \left[1 + \frac{\upsilon_a}{\upsilon} T \left(2 \frac{dJ}{dT} + T \frac{d^2 J}{dT^2} \right) \right].$$ (29)

At high temperatures $(T \gg \varepsilon)$ for the Sutherland potential (7), $J = (1/3)(\varepsilon/T) + (1/18)(\varepsilon/T)^2$, so that the heat capacity with account of the main correction for the long-range interaction takes the form

$$C_V = \frac{3}{2} N \left(1 + \frac{\upsilon_a}{\upsilon} \frac{\varepsilon^2}{9T^2} \right).$$ (30)

Then for energy, we have

$$E = \frac{3}{2} NT \left(1 - \frac{\upsilon_a}{3\upsilon} \frac{\varepsilon}{T} - \frac{\upsilon_a}{9\upsilon} \frac{\varepsilon^2}{T^2} \right).$$ (31)

It is obvious that $C_V = -(\partial E/\partial T)_{V, N}$.

4. CONCLUSIONS

Since the potential of repulsion of atoms at small distances is usually known poorly, it is quite acceptable to use the model of hard spheres to take into account the short-range correlations in systems of many particles. Along with a short-range repulsion, the realistic potential contains a smooth component describing the interaction of atoms at long distances. The description of contribution of the long-range interaction to the thermodynamic quantities of dilute systems has been considered in this work.

The method of decomposition of the pair potential of interaction between particles into the hard core and the long-range part, proposed in this paper, is important in connection with the question of possibility of using the self-consistent field method in the theory of dense sys-

tems. The idea of using the self-consistent field method, which allows to effectively describing phase transitions, in the theory of solids was proposed many years ago by Vlasov [8]. Many leading physicists subjected Vlasov's approach to criticism. Nevertheless, the self-consistent field method, although without firm justification, was later employed as well to construct the statistical theory of the crystal state [9, 10] and the thermodynamic perturbation theory [11].

Now, apparently, we can conclude that both Vlasov and his critics were right. Obviously, the short-range correlations of particles cannot be described in the framework of the self-consistent field model, but it is natural to consider them in the framework of the model of hard spheres. The interaction of atoms through a smooth long-range part of the potential can now be taken into account by the self-consistent field method. Therefore, the decomposition of the potential into the short-range and long-range parts and the using of the mean-field theory to take into account the smooth part of the interaction may be important for the further development of the theory of dense gases, liquids, and solids.

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