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THEORETICAL AND MATHEMATICAL PHYSICS

A New Method to Obtain the Carnahan–Starling Equation and Its Generalization

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Abstract—We obtain the Carnahan–Starling equation for a system of hard spheres using the Euler method of accelerated series convergence. For this purpose, the virial series is transformed into a new series with coefficients that differ slightly from each other, even when considering the eleven currently known virial coefficients. The method of accelerated convergence was applied to this series; it allowed us to obtain the Carnahan–Starling equation. In this work, this equation is derived for the first time using the method of accelerated convergence. It is generalized to accurately reproduce all of the known virial coefficients and the asymptotic behavior of the free energy at high densities. This also makes it possible to describe a metastable region with a high degree of accuracy and to obtain the equation of state for a homogeneous system of hard spheres with the accuracy of a computer experiment.

Keywords: classical ensemble theory, thermodynamic functions, equations of state, phase transitions.

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INTRODUCTION

The Carnahan–Starling equation for the equation of state of a system of hard spheres [1] was obtained nearly 50 years ago; it resolved the problem of the description of dense liquids. This equation of state made it possible to account for repulsive forces of particle interactions with high accuracy, whereas the attraction part of the interaction potential could be calculated rather simply by that time.

The passage of time has shown [2, 3] how successful the semiempirical approximation using the six available virial coefficients has become [4] (in fairness it should be noted that the seventh virial coefficient was also well known [5] to the authors of [1]). Even with the currently known eleven virial coefficients, this approximation has not lost its relevance. Among simple analytical equations of state the Carnahan–Starling equation is still the most accurate one, with the exception of the metastable region.

In [6], a method was proposed based on using the structure of the Carnahan–Starling equation which allows one to precisely reproduce all the known virial coefficients. It was generalized to molecular systems with positively defined interaction potential between the particles. In this case, unlike obtaining the Carnahan–Starling equation [1], the expression for free energy was used as a starting point instead of the thermal equation of state. However, an open issue remained relating to consistently obtaining the Carnahan–Starling equation. This issue not only has a general theoretical meaning, but also leads to new numerical results.

To solve the problems of statistical thermodynamics one has to use a perturbation theory series. In this case, the calculation of each next term of the series faces significant mathematical difficulties. Moreover, the obtained series converge very slowly for many of the most interesting regions of the phase diagram of a substance.

For this reason, the problem of convergence of the series arises, namely their transformation into another series with the same sum as the original, but with faster convergence [7–12]. Despite the great advances in calculating virial coefficients, their number is quite limited; this determines the relevance of using the methods of accelerated convergence.

Currently, the number of known virial coefficients for a system of hard spheres equals eleven and is eight for systems with the Lennard–Jones interaction potential; in the last 50 years the accuracy of the calculation of these virial coefficients has increased significantly [13–36]. For more complex interaction potentials the number of the known virial coefficients is still lower. In this regard, the use of methods of accelerated series convergence of perturbation theory is absolutely essential when using the virial series in more sophisticated variants of perturbation theory [37] to describe the state of matter at high densities.

The existing methods of the accelerated convergence of the perturbation theory series in statistical thermodynamics can be divided into three groups. These are primarily mathematical methods of accelerated convergence. They are based on the purely mathematical properties of the series, which are either known originally or their presence is assumed. Among the mathematical methods for accelerated convergence one can mention the Kummer and Euler methods, the method of Pade approximants, and many others [8].

The essence of the physical techniques of accelerated convergence lies in the fact that on the basis of physical considerations we turn from the functions with slowly converging perturbation series to the functions for which the perturbation series converge faster [12]. The main task of statistical thermodynamics is reduced to the calculation of the statistical integral. For real interaction potentials its properties help to identify those functions for which the perturbation series converge faster.

To accelerate the convergence of a perturbation series on the basis of physical considerations one should also take the dimensionality of space into account. It is necessary to use the representation of the number of nearest neighbors, the behavior of the system at large densities, including the metastable region, and the region of the ordered phase, as well as the features in the behavior of various thermodynamic functions [3, 38–50]. An important role here is played by the choice of the main approximation. A sufficiently exact equation of the state of the system of hard spheres is necessary in the case of non-equilibrium processes for calculating transport coefficients for dense gases within the Boltzmann–Enskog theory [51–54].

The combined methods of the accelerated convergence of the perturbation series are more general. Within this approach, a transition to the functions for which the perturbation series converges quickly is performed based on physical considerations and mathematical convergence acceleration techniques are then applied to it [9].

In this paper, obtaining the Carnahan–Starling equation is reduced to an application of Euler's method for accelerated convergence of a series obtained on the basis of a series in the powers of the free-energy density. Such a series has the property that its coefficients slightly differ from each other. Roughly speaking, this series behaves like a geometric progression. A single application of the Euler method [7, 8] to this series, taking only the second virial coefficient into account (and using information about the known virial coefficients) allows one to obtain the Carnahan–Starling equation.

With subsequent allowance for all of the known virial coefficients one can find the equation of state that describes a stable phase with the accuracy of a computer experiment [3]. The metastable phase is also described well by this equation. To improve the agreement between theory and experiment in the metastable region, the asymptotic behavior of the expression for the free energy of the system was taken into account [6]. As a result, full agreement between the theoretical data and those of the computer experiment was obtained.

THE VIRIAL EXPANSION FOR A SYSTEM OF HARD SPHERES

Currently, eleven virial coefficients for the system of hard-spheres are known, which were found numerically [2]. The first four of these are calculated in the exact form. This makes it possible to obtain the equation of state of the system with a high degree of accuracy at low and intermediate densities. In the general case, the series expansion of the compressibility has the form

$$z = \frac{pV}{NkT} = 1 + \sum_{i=2}^{\infty} b_i \rho^{i-1}. \tag{1}$$

Here, V is the volume of the system, N is the number of particles in it, T is the absolute temperature, p is the pressure, k is the Boltzmann constant, b_i are the virial coefficients; and $\rho = N/V$ is the density.

We proceed in expression (1) to the dimensionless variables

$$z = 1 + \sum_{i=2}^{\infty} \bar{b}_i y^{i-1}. \tag{2}$$

In expansion (2) for compressibility $y = \pi\sigma^3\rho/6$, $\bar{b}_i = b_i(6/\pi\sigma^3)^{i-1}$, and σ is the diameter of hard spheres.

For further treatment, it is convenient to use the following expression for the free energy of a system of hard spheres:

$$F = F_0 + NkT\varphi. \tag{3}$$

In this expression F_0 is the free energy of an ideal gas,

$$\varphi = \sum_{i=2}^{\infty} \frac{\bar{b}_i}{i-1} y^{i-1}. \tag{4}$$

Figure 1 shows the dependence of the coefficient $\varphi_i = \frac{\bar{b}_i}{i-1}$ of series (4) on the virial coefficient number i for the eleven known virial coefficients. This dependence can be represented as a linear one with a good degree of accuracy.

Hence, it is easy to see that for the function

$$\chi = \int_0^y \varphi(t) t^2 dt = \sum_{i=2}^{\infty} \frac{\bar{b}_i}{(i-1)(i+2)} y^{i+2} \tag{5}$$

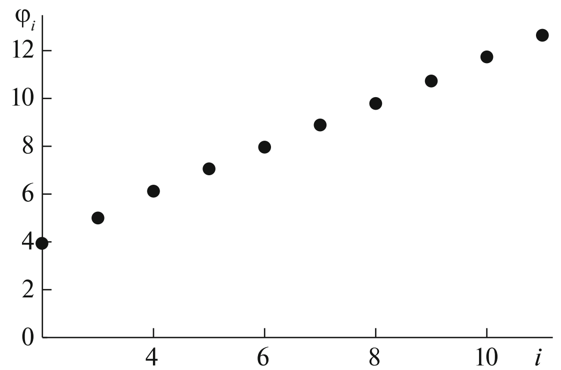

Fig. 1. The coefficients of expansion of the function φ depending on their numbers.

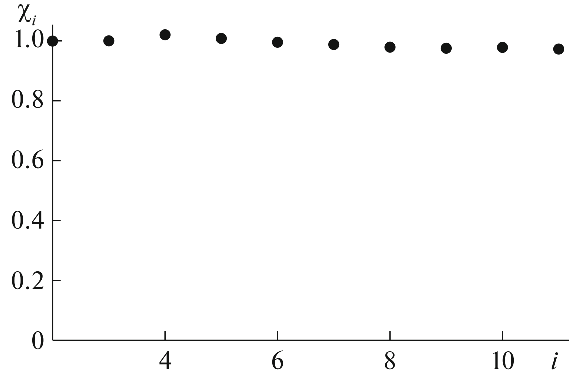

Fig. 2. The coefficients of expansion of the function χ depending on their numbers.

the coefficients $\chi_i = \dfrac{\bar{b}_i}{(i-1)(i+2)}$ are close to 1 (see Fig. 2). It is worthwhile to draw attention to a slight decrease of coefficients χ_i starting from the number $i = 5$. In essence, two basic features in the behavior of the virial series of a system of hard spheres are exhibited. The first is that at $i \leq 5$ the coefficients χ_i exceed or equal 1, whereas all known coefficients are less than 1 at $i > 5$. The success of the Carnahan–Starling equation is due to the fortuitous behavior of the coefficients χ_i in an interval close to 1 [1, 6]. The second feature is that, since the number of coefficients χ_i that are less than 1 is considerable, and integrally the Carnahan–Starling equation describes compressibility well, the coefficients χ_i must exceed 1 starting from a certain number. This feature is caused by the behavior of the statistical integral at high densities. We will be able to use it for a quantitative description of the equation of state of hard spheres at high densities, including the metastable region [12].

2. THE METHOD OF THE ACCELERATED CONVERGENCE OF THE FUNCTION χ

Since the series coefficients for the function χ are close to 1, the Euler method of accelerated convergence can be applied to this series [7]. As a result, for χ in (5) we obtain

$$\chi = \frac{y^4\left(1 + \sum_{i=4}^{\infty} c_i y^{i-1}\right)}{1-y}, \tag{6}$$

where

$$c_i = \frac{\bar{b}_i}{(i+2)(i-1)} - \frac{\bar{b}_{i-1}}{(i+1)(i-2)}. \tag{7}$$

In deriving (6) we took the fact into account that $\bar{b}_2/4 = 1$ and $\bar{b}_3/10 = 1$.

Having calculated coefficients c_i ($i \geq 4$) according to (7), we obtain the function χ from (6). This allows us to obtain the function φ from (5)

$$\varphi = \frac{d\chi(y)}{dy}/y^2 = \frac{4y - 3y^2 + 6c_4y^3 + \sum_{i=4}^{\infty} d_i y^i}{(1-y)^2}, \tag{8}$$

where

$$d_i = (i+3)c_{i+1} - (i+1)c_i. \tag{9}$$

As a result, the free energy (3) of the system, according to (8) and (9), is completely determined.

Using (3) with allowance for (8) we find the expression for compressibility

$$z = 1 + y\frac{d\varphi}{dy}$$

$$= 1 + \frac{4y - 2y^2 + 18c_4y^3 + (28c_5 - 26c_4)y^4 + \sum_{i=4}^{\infty} e_i y^{i+1}}{(1-y)^3}, \tag{10}$$

where

$$e_i = (i+1)d_{i+1} - (i-2)d_i. \tag{11}$$

To obtain the Carnahan–Starling equation, we put $c_i = 0$ ($i \geq 4$). This approximation is satisfied with a good degree of accuracy for all currently known virial coefficients.

In this case one obtains from (6)

$$\chi = \frac{y^4}{1-y}. \tag{12}$$

Using (12) and (8) the function φ takes the form

$$\varphi = \frac{4y - 3y^2}{(1-y)^2}. \tag{13}$$

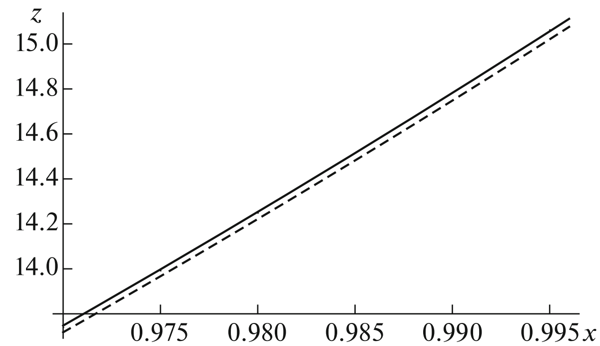

Fig. 3. The dependence of the compressibility on the density in the metastable region of the system of hard spheres for Carnahan–Starling equation (14) (dotted line), and calculated by Eq. (18) with allowance for eleven virial coefficients. The points show the data of the computer experiment.

According to (10), (11), and (13), the expression for compressibility is given by

$$z = 1 + \frac{4y - 2y^2}{(1-y)^3} = \frac{1 + y + y^2 - y^3}{(1-y)^3}. \tag{14}$$

Expression (14) is the Carnahan–Starling equation.

In the general case $c_i \neq 0$ for $i \geq 4$, in order to determine the compressibility we should use (10), restricting the infinite series by a finite one whose terms are determined by the known virial coefficients.

Expression (10) for compressibility yields results that are in agreement with the data of computer experiment in the limits of their accuracy in the stable region. The same agreement can be obtained in the metastable region with allowance for the logarithmic asymptotics of the free-energy expression at large densities [6]. For this purpose, the function φ in expression (3) for the free energy is written in the form

$$\varphi = -m(y)\ln(1 - ay), \tag{15}$$

where $a = 6/\sqrt{2\pi}$, and $m(y)$ is a new function that has the meaning of a half number of nearest neighbors [6].

To determine the form of function $m(y)$ we take the fact into account that in the region of the stable phase the function φ can be calculated within the generalized Carnahan–Starling approximation, according to (8). With allowance for this, it is natural to represent $m(y)$ in the form

$$m(y) = \frac{\psi(y)}{(1-y)^2}, \tag{16}$$

where we seek the function $\psi(y)$ in the form

$$\psi(y) = p_0 + p_1 y + p_2 y^2 + p_3 y^3 + \dots. \tag{17}$$

The coefficients p_i in (17) are found from the condition of asymptotic coincidence of the function φ calculated from (15) with allowance for (16) and (17), and the function calculated by (8). The number of terms in series (17) is restricted by the condition that the function $m(y)$ monotonously increases, since the effective number of nearest neighbors increases with increasing density.

Expressions (3) and (15)–(17) completely determine the free energy in the given approximation. Using (3) and (10) the expression for compressibility takes the form

$$\begin{aligned} z &= 1 + \frac{amy}{1-ay} - y\frac{dm}{dy}\ln(1-ay) = 1 + \frac{a\psi y}{(1-ay)(1-y)^2} \\ &- \frac{(2p_0 + p_1)y + (p_1 + 2p_2)y^2 + 3p_3y^3 - (p_3 - 4p_4)y^4 - \dots}{(1-y)^3}\ln(1-ay). \end{aligned} \tag{18}$$

Figure 3 shows the dependences of the compressibility on the density in the metastable region of a system of hard spheres calculated by the Carnahan–Starling equation (14) (dotted line) and equation (18) (solid line) with allowance for eleven virial coefficients. The points denote the data of the computer experiment [3], $x = 6y/\pi$. One can clearly note the improving agreement of theoretical data calculated from (18) with those of the computer simulation as compared to the Carnahan–Starling equation (14).

For the stable phase, equations (10) and (18) lead to results that differ in the limits of accuracy of the computer experiment. In this case one can use a simpler though less general expression (10).

CONCLUSIONS

In this work, for the first time, the Carnahan–Starling equation of state of a system of hard spheres has been obtained based on the use of Euler's method of accelerated series convergence. This method can be generalized to accurate calculations with an arbitrary number of precisely known virial coefficients. As a result, the obtained expression (10) for compressibility reproduces the data of computer simulation within its accuracy.

For the metastable region, a misalignment becomes noticeable with increasing density in the two-phase region, despite relatively good coincidence. The reason for this can be seen already when analyzing the behavior of the first eleven known virial coefficients compared with the same coefficients found in the main Carnahan–Starling approximation, and taking the behavior of the statistical integral at high densities into account.

The Carnahan–Starling equation was obtained based on a successful choice of the interpolation formula for virial coefficients, which describes the virial coefficients well. This has led to the success of this approach. Numerous attempts have been made to generalize the Carnahan–Starling approximation [38, 55]. However, this equation does not describe the asymptotic behavior of the statistical integral at high densities. According to (16), in this approximation, the number of nearest neighbors begins to diminish starting from a certain density and reaches physically meaningless values. Therefore, to obtain consistent results one has to restrict the number of terms of the series that must be taken into account. The character of the dependence of the effective number of nearest neighbors serves as a physical criterion.

As a result, we obtained formula (18) for compressibility, which describes both the stable and metastable areas of the phase diagram well. Thus, the results make it possible to claim that this method allows one to obtain the generalized Carnahan–Starling equation (18), correctly reproduces all of the known virial coefficients, and describes the phase diagram of a homogeneous system of hard spheres within the accuracy of a modern computer experiment.

This approach is applicable for positively defined potentials of a general form when quantum effects are taken into account [56]. It can be generalized to the systems in external fields and mixtures of different systems.

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