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OPTICS AND SPECTROSCOPY

APPLICATION OF PERTURBATION THEORY TO A MIXTURE OF HYDROGEN ATOMS AND MOLECULES WITH THE MORSE INTERMOLECULAR INTERACTION POTENTIAL

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The thermodynamic parameters of the two-component mixture of hydrogen atoms and molecules are calculated on the basis of perturbation theory with the use of the basic system of hard spheres. To eliminate the nonadditivity of hard sphere diameters and to obtain the best agreement of the calculated thermodynamic parameters with the Monte Carlo data, different schemes of subdivision of the interaction potential of hydrogen atoms and molecules into the basic and perturbing components are investigated.

Keywords: single-component fluid, Monte Carlo and molecular dynamics methods, variational perturbation theory, excessive Helmholtz energy, thermodynamic states, equation of state, intermolecular Morse potential.

INTRODUCTION

Knowledge of the thermodynamic properties of fluids (gases and liquids under critical or supercritical conditions) and fluid mixtures is necessary for modeling of the atmospheres of massive planets, magma in the internal Earth's layers, various reacting chemical mixtures, and condensed explosive detonation products. Of special practical importance are thermodynamic calculations of such systems at high densities and pressures.

Considerable advances have been made in the last decades in the study of equations of state for dense fluids and liquid gases, such as He, Ar, Ne, H_2, N_2, and CH_4 in the vicinity of the triple point at which kT/ε is about unity. The existing methods and the integral [1], variational [2], and perturbation theories [3, 4] reproduce well the thermodynamic properties of dense atomic and single-component molecular fluids for wide ranges of pressure and temperature variations and are used to derive equations of fluid state. Modeling by the Monte Carlo (MC) method [5] allows the state parameters to be reproduced exactly for fluids and their mixtures. It is conventionally used to compare calculated results with the data obtained in the context of the above-enumerated theories to substantiate their applicability.

Attempts of generalizing the existing single-component fluid theories to a description of thermodynamic properties of binary and multicomponent fluid mixtures [6–9] are less successful than the results of application of these theories to the single-component systems. By the present time, procedures for calculating the state parameters of binary and triple mixtures with the Lennard–Jones interparticle interaction potential have been developed [6–9]. However, only a few attempts of application of other interparticle interaction potentials to calculations of thermodynamic states of fluid mixtures are known (for example, see [6–9]).

In the present work, the applicability of the perturbation theory to a description of the two-component fluid mixture of hydrogen atoms and molecules interacting with the Morse potential is discussed. The main point of any perturbation theory is subdivision of the potential $\varphi(r)$ of the examined system (that is, the system for which the excessive thermodynamic properties are calculated) into two components: reference component $\varphi^{\mathrm{ref}}(r)$ that characterizes

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the molecular interaction potential in a certain basic system and small perturbing component $\varphi^{\mathrm{per}}(r)$. As a basic system, we take advantage of the system of hard spheres conventionally used to study dense fluids.

The thermodynamic perturbation theories differ by the method of interaction potential subdivision into the basic and perturbing components as well as by the criterion used to estimate the hard sphere diameters. Weeks, Chandler, and Andersen (WCA) [10, 11] used the hard sphere potential as a basic repulsive potential and proposed a thermodynamic criterion (equality of the compressibility factors of the basic system and equivalent hard-sphere fluid) to calculate the hard sphere diameters. This approach describes well the thermodynamic properties of single-component dense fluids [10–12].

However, the WCA perturbation theory has some disadvantages at high temperatures. First, the application of the basic hard-sphere potential cannot be justified at temperatures at which it must be replaced by a softer repulsive potential. Second, for the hard sphere packing factor near the melting transition ($\eta > 0.4$), the WCA criterion overestimates the hard sphere diameters and leads to the metastability of the basic system. This was also pointed out by Kang *et al.* [13] for single-component systems. Therefore, for the most part the hard sphere diameters do not satisfy the additivity condition

$$R_{12} = \frac{1}{2}(R_{11} + R_{22}) \tag{1}$$

for the hard-sphere system, where R_{11} and R_{22} are the effective hard sphere diameters. As a result, the thermodynamic properties of the two-component fluids calculated by the WCA method typically deviate by 10–15% from the MC data and yield physically unjustified results at high densities of interest to us.

In the present work, different schemes of potential subdivision into the basic and perturbing components are used to calculate the thermodynamic properties of a two-component fluid to compare them with results of modeling by the Monte Carlo method and to choose the most correct scheme of potential subdivision that can further be used to calculate the thermodynamic properties of the two-component fluids with different interparticle interaction potentials.

By analogy with [14], the influence of the potential subdivision scheme on the accuracy of calculating the thermodynamic parameters is analyzed on the example of the two-component mixture of hydrogen atoms and molecules with the Morse interparticle interaction potential. To compare the calculated thermodynamic properties of binary mixtures of hydrogen atoms and molecules, the results obtained in [14] by the MC method for the Morse potential are used.

PERTURBATION THEORY

Single-component fluid

In the context of the perturbation theory, the Helmholtz free energy of the single-component fluid can be written as

$$F = F_{HS} + F_{HTA} + F_{ho}\,, \tag{2}$$

where F_{HS} is the free energy of the basic hard-sphere fluid. The second term in Eq. (2) describes the excessive energy caused by the intermolecular interaction; it is determined by the following expression:

$$\frac{\beta F_{HTA}}{N} = \frac{\rho}{2}\int_{0}^{\infty}\beta\varphi^{\mathrm{pert}}(r)g(r)d^{3}r\,,$$

where $g(r)$ is the radial hard-sphere distribution function, $\beta^{-1} = kT$, and $\rho = N/V$ is the density. The term F_{ho} is small compared to F_{HS} and F_{HTA} and is neglected below [15].

Equation (2) must be supplemented with a description of the scheme of interaction potential subdivision into the reference and perturbing components together with the condition of determining the hard sphere diameter R. The WCA criterion requires that the compressibility factors of the hard-sphere and basic systems were equal. The compressibility χ is described by the equation

$$\frac{\rho\chi}{\beta} = 1 + \rho\int[g(r) - 1]d^3r. \tag{3}$$

If we assign $y^{\mathrm{ref}}(r)$ in the form

$$g^{\mathrm{ref}}(r) = y^{\mathrm{ref}}(r)\exp[-\beta\varphi^{\mathrm{ref}}(r)],$$

the criterion will assume the following form:

$$\int[y^{HS}(r)\exp^{-\beta\varphi^{HS}(r)} - 1]d^3r = \int[y^{\mathrm{ref}}(r)\exp^{-\beta\varphi^{\mathrm{ref}}(r)} - 1]d^3r. \tag{4}$$

After approximation of $y^{\mathrm{ref}}(r)$ on the right side of Eq. (4) by the function $y^{HS}(r)$ with allowance for the definition of the hard-sphere potential

$$\varphi^{HS}(r) = \begin{cases} \infty, \ r < R, \\ 0, \ r > R, \end{cases}$$

we can write Eq. (4) in the form

$$I = \int_0^R y^{HS}(r)\exp[-\beta\varphi^{\mathrm{ref}}(r)]d^3r + \int_R^\lambda g^{HS}(r)\{\exp[-\beta\varphi^{\mathrm{ref}}(r)] - 1\}d^3r. \tag{5}$$

Equation (5) for the hard-sphere diameter R can be solved numerically for known values of the density ρ and temperature T.

In the context of the perturbation theory, the potential $\varphi(r)$ of the examined system is the sum of the two components, where $\varphi^{\mathrm{ref}}(r)$ is its dominating component representing the molecular interaction potential in a basic system and $\varphi^{\mathrm{pert}}(r)$ is its small perturbation:

$$\varphi(r) = \varphi^{\mathrm{ref}}(r) + \varphi^{\mathrm{pert}}(r). \tag{6a}$$

Here

$$\varphi^{\mathrm{ref}}(r) = \begin{cases} \varphi(r) - F(r,\lambda), \ r < \lambda, \\ 0, \ r > \lambda, \end{cases} \tag{6b}$$

$$\varphi^{\mathrm{pert}}(r) = \begin{cases} F(r,\lambda), \ r < \lambda, \\ \varphi(r), \ r > \lambda. \end{cases} \tag{6c}$$

The potential subdivision point λ and the functional form of the smoothing potential $F(r, \lambda)$ are arbitrary given that $\varphi^{\mathrm{ref}}(r)$ is repulsive in character. For example, in the WCA scheme, $\lambda = r^*$, where r^* is the position of the potential minimum (that is, $\varphi'(r^*) = 0$, where the prime denotes differentiation with respect to r) and $F(r, \lambda) = \varphi(\lambda)$. However, when the packing factor is close to its frozen value for hard spheres ($\eta = 0.494$), the reference potential becomes too repulsive thereby causing the metastability of the basic system in the fluid phase. For this reason, Kang *et al.* [13] suggested the potential subdivision scheme different from the WCA scheme, in which $\lambda = \min(r^*, a_{fcc})$, where $a_{fcc} = 2^{1/6}/\rho^{1/3}$ is the equivalent distance for the *fcc* lattice, and

$$F(r,\lambda) = \varphi(\lambda) + (r-\lambda)\varphi'(\lambda)\,. \tag{7}$$

This form is reduced to the WCA form for low densities when $a_{fcc} > r^*$. For densities higher than those lying on the melting curve and for temperatures exceeding $kT/\varepsilon = 100$, this scheme yields the calculated results that are in agreement with the MC data for single-component fluids whose molecules interact with the Lennard–Jones, e^{-6}, and inverse power-law potentials.

Two-component mixtures

The WCA criterion for a binary system has the form

$$\sum_{i,j=1}^{2} x_i x_j I_{ij} = 0\,,\ i,j = 1, 2, \tag{8}$$

where x_i and x_j are the mole fractions of the ith and jth components of the mixture, respectively, and I_{ij} corresponds to integral I given by Eq. (5):

$$I_{ij} = \int_0^{R_{ij}} y_{ij}^{HS}(r)\exp[-\beta\varphi_{ij}^{\mathrm{ref}}(r)]d^3r + \int_{R_{ij}}^{\lambda_{ij}} g_{ij}^{HS}(r)\{\exp[-\beta\varphi_{ij}^{\mathrm{ref}}(r)]-1\}d^3r\,. \tag{9}$$

To change integration limits in the second term of Eq. (9), the condition $\varphi_{ij}^{\mathrm{ref}}(r \ge \lambda_{ij}) = 0$ has been used. Equation (9) for the two-component system has generally no unique solution for $\{R_{11}, R_{12}, R_{22}\}$ [16], but the system of three paired equations

$$I_{ij} = 0 \tag{10}$$

has a unique solution. However, the hard-sphere diameters calculated from Eq. (10) do not generally satisfy condition (1) required to provide the additivity of the basic hard-sphere system. This discrepancy can be eliminated by solving equations

$$I_{11} = I_{22} = 0 \tag{11}$$

for R_{11} and R_{22} and subsequent choice of the potential $\varphi_{12}^{\mathrm{ref}}(r)$ so that additivity condition (1) was satisfied and

$$I_{12} = 0\,. \tag{12}$$

Kahl and Hafner [17], who suggested this idea for the first time, have retained the WCA form and used the potential subdivision point λ_{12} as an adjusting parameter to meet condition (12). In this case, the function $I_{12}(\lambda_{12})$ has a minimum at $\lambda_{12} = r_{12}^*$. Hence there exist two solutions of Eq. (12) on different sides of r_{12}^* for $I_{12}(\lambda_{12} = r_{12}^*) < 0$. Proceeding from the condition that $\varphi_{12}^{\mathrm{ref}}(r)$ retains purely repulsive in character, we must choose the root $\lambda_{12} < r_{12}^*$.

Unfortunately, the condition $I_{12}(\lambda_{12} = r_{12}^*) < 0$ is not always satisfied, because it depends on the nature of the potentials $\varphi_{ij}(r)$ and on the thermodynamic state. Figure 1 shows the typical behavior of $I_{12}(\lambda_{12} = r_{12}^*)$ as a function of the density for the mixture of hydrogen atoms and molecules (curve $N = 0$). The qualitative behavior of the curve is independent of the temperature. At low densities at which $I_{12}(\lambda_{12} = r_{12}^*) > 0$, the corresponding packing factor is

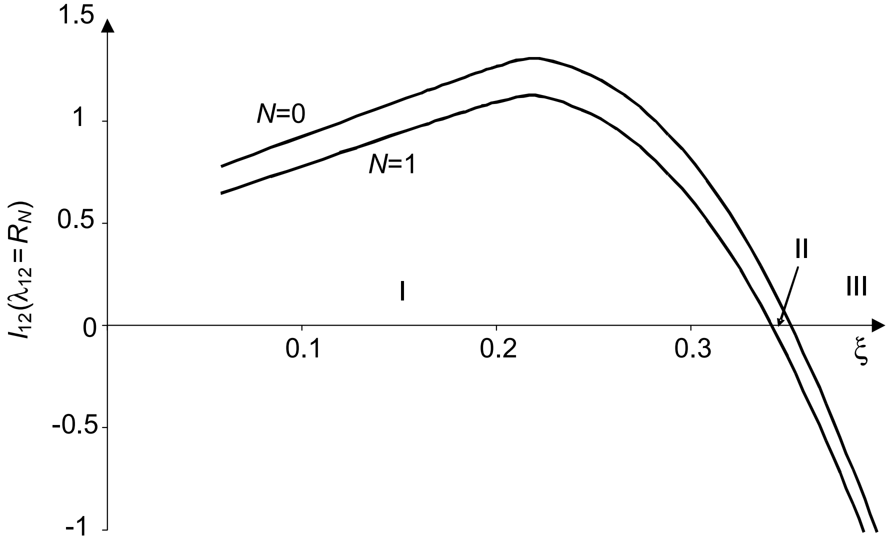

Fig. 1. Behavior of the function $I_{12}(\lambda_{12}=R_N)$ versus the hard-sphere packing factor ξ at $T = 1000$ K. Curves with the indicated N values show the dependences drawn with the polynomial smoothing potential of degree N (see Eq. (32)). The Roman numbers indicate three regions of density variations discussed in the text.

$\eta \le 0.35$, and Eqs. (1) and (12) of the Kahl–Hafner scheme are simultaneously violated. The physical reason is that the reference potential $\varphi_{12}^{\text{ref}}(r)$ is weakly repulsive in this region. In this case, the pressure and the internal energy of the system are discontinuous when $I_{12}(\lambda_{12} = r_{12}^*)$ changes its sign (Fig. 1). For this reason, the results obtained do not agree with the MC data. To eliminate these disadvantages, the potential subdivision scheme suggested in [14] and aimed at making $\varphi_{12}^{\text{ref}}(r)$ harder was used in the present work.

PROCEDURE FOR CALCULATING THE THERMODYNAMIC PARAMETERS OF THE MIXTURE OF HYDROGEN ATOMS AND MOLECULES

In the present work, different subdivision schemes of the interaction potentials $\varphi_{ij}(r)$ of the two-component fluid comprising hydrogen atoms and molecules ($x_{\text{H}} = x_{\text{H}_2} = 0.5$) into the basic and perturbing components were used. The choice of the suitable scheme of interaction potential subdivision into the reference and perturbing components involves the choice of the subdivision point and functional for the smoothing potential $F(r, \lambda)$ that must provide the additivity of the basic system and good agreement of the calculated results with the MC data.

For this purpose, the simple Morse potentials for three interaction types $\varphi_{\text{H}_2-\text{H}_2}$, $\varphi_{\text{H}-\text{H}_2}$, and $\varphi_{\text{H}-\text{H}}$ were used:

$$\varphi_{ij}(r) = \varepsilon_{ij}\left\{\exp[-2s_{ij}(r - r_{ij}^*)] - 2\exp[-s_{ij}(r - r_{ij}^*)]\right\}. \tag{13}$$

The coefficients ε_{ij}, s_{ij}, and r_{ij}^* tabulated in Table 1 were borrowed from [14]. The potentials $\{\varphi_{11}, \varphi_{12}, \varphi_{22}\}$ are nonadditive; therefore, $\varphi_{12}(r)$ differs significantly from the simple interpolation between $\varphi_{11}(r)$ and $\varphi_{22}(r)$. Hence, this case provides a severe test of the suggested subdivision scheme.

The procedure used to calculate the thermodynamic parameters of the two-component fluid was the following. First Eq. (11) for R_{11} and R_{22} was solved. The approximation by cubic polynomials suggested by Grundke and Henderson [18] was used for the functions $y_{ij}^{HS}(r)$ with $r < R_{ij}$. To calculate the radial hard-sphere functions $g_{ij}^{HS}(r)$, the procedure based on the inversion of the Laplace transforms of functions $rg_{ij}(r)$ obtained by Lebowitz [19] from the Percus–Yevic equation was used. However, the agreement between the functions $g_{ij}^{PY}(r)$ obtained from the Percus–Yevic equation and the exact hard-sphere distribution function $g_{ij}^{MC}(r)$ obtained in computer experiments by the Monte

TABLE 1. Parameters of the Morse Potential for $\varphi_{\mathrm{H_2-H_2}}$, $\varphi_{\mathrm{H-H_2}}$, and $\varphi_{\mathrm{H-H}}$

Interaction type	ε, K	r^*, Å	s, Å^{-1}
H–H	20.2	3.28	1.436
H–H$_2$	25.5	3.36	1.323
H$_2$–H$_2$	32.2	3.44	1.568

Carlo method was unsatisfactory. Therefore, in the present work, by analogy with the Verlet–Weis procedure [20], approximate expressions for the radial hard-sphere distribution functions of the form

$$g_{ij}(r,\{R\},\{\rho\}) = H(r-R_{ij})g_{ij}^{\mathrm{PY}}(r,\{R^w\},\{\rho\}) + \Delta g_{ij}(r)\,, \tag{14}$$

$$H(x) = \begin{cases} 1, & x \ge 0, \\ 0, & x < 0, \end{cases}$$

$$R_{ij}^w = R_{ij}(1-\xi/16)^{1/3}\,,$$

$$\Delta g_{ij}(r) = \frac{A_{ij}}{r}\exp[-\mu_{ij}(r-R_{ij})]\cos\mu_{ij}(r-R_{ij})\,, \tag{15}$$

derived by solving the Percus–Yevic equations with the adjusting term $\Delta g(r)$ were used for the single-component system to obtain the best agreement with the results of modeling by the MC method. The parameters A_{ij} were determined from values of the exact functions $g_{ij}(r)$ at the contact points:

$$\frac{A_{ij}}{R_{ij}} = g_{ij}(R_{ij},\{R\},\{\rho\}) - g_{ij}^{PY}(R_{ij},\{R^w\},\{\rho\}), \quad ij = 11,\ 12,\ 22\,. \tag{16}$$

To calculate the function $g_{ij}(R_{ij})$ entering into Eq. (16), the approximation scheme was used to calculate exact values of $g_{ij}(R_{ij})$ at the contact points according to the Carnahan–Starling rule [21, 22]

$$g_{ij}^{CS}(R_{ij},\xi) = \frac{1}{3}g_{ij}^{\mathrm{PY}}(R_{ij},\xi) + \frac{2}{3}g_{ij}^{\mathrm{SPT}}(R_{ij},\xi)\,.$$

Here $g_{ij}^{PY}(R_{ij})$ are values of the radial distribution function at the contact points obtained from the Lebowitz solution for the hard-sphere mixtures, and $g_{ij}^{SPT}(R_{ij})$ are calculated in the context of scaled particle theory (SPT) [23].

The parameters μ_{ij} were determined from the following expression:

$$\mu_{ij}R_{ij} \approx \frac{24A_{ij}/R_{ij}}{\xi_w g_{ij}^{\mathrm{PY}}(R_{ij}^w,\{R^w\},\{\rho\})}\,.$$

The system of equations $I_{11} = 0$ and $I_{22} = 0$ was solved using the Newton–Raphson algorithm with the diameters calculated in the context of the Barker–Henderson theory [24]

$$R_{ii} = \int_0^{\lambda_{ij}} \{1-\exp[-\beta\varphi_{ii}^{\mathrm{ref}}(r)]\}dr$$

as initial values. Then Eq. (12) was solved to determine the free parameter of the chosen subdivision scheme for the potential $\varphi_{12}(r)$ using condition (1) for R_{12}. Having calculated the hard sphere diameters and the free potential parameter for the chosen potential subdivision scheme, we can calculate the free Helmholtz energy from the formula

$$\frac{\beta F^{ex}}{N} = \frac{\beta F_{HS}}{N} + \frac{\rho}{2} \sum_{i,j=1}^{2} x_i x_j \int_0^{\infty} g_{ij}^{HS}(r) \beta \varphi_{ij}^{\text{pert}}(r) d^3 r \ . \tag{17}$$

Here F_{HS} is the energy of the Mansoori hard-sphere mixture [21], the superscript "*ex*" designates their excessive number, and subscripts 1 and 2 refer to H and H_2, respectively. The integral in Eq. (17) was estimated numerically in [14]. However, this method requires long computational time increasing rapidly with the integration variable r. Therefore, in the present work we have suggested the procedure that significantly simplifies calculations and allows the agreement to be obtained with the MC data better than in [14].

Let us consider the second term of Eq. (17) comprising the integral for $i, j = 1, 2$:

$$F_{ij}^{ex} = 2\pi\rho\beta \int_0^{\infty} g_{ij}(r) \beta \varphi_{ij}^{\text{pert}}(r) d^3 r = F_{1,ij} + F_{2,ij} \ , \tag{18}$$

where

$$F_{1,ij} = 2\pi\rho\beta \int_{R_{ij}}^{\infty} \varphi_{ij}(r) g_{ij}(r) r^2 dr \ , \tag{19}$$

$$F_{2,ij} = -2\pi\rho\beta \int_{R_{ij}}^{\lambda_{ij}} \varphi_{ij}^{\text{ref}}(r) g_{ij}(r) r^2 dr \ . \tag{20}$$

Taking into account that potential (13) represents the sum of two terms one of which describes repulsion of molecules and the other characterizes their attraction, free energy (19) can be written as

$$F_{1,ij} = F_{1,ij}^{r} + F_{1,ij}^{a} \ , \tag{21}$$

where

$$F_{1,ij}^{r} = 2\pi\rho\beta\varepsilon_{ij} e^{2 s_{ij} r_{m,ij}} \int_{R_{ij}}^{\infty} \exp(-2 s_{ij} r) r^2 g_{ij}(r) dr \ , \tag{22}$$

$$F_{1,ij}^{a} = -4\pi\rho\beta\varepsilon_{ij} e^{s_{ij} r_{m,ij}} \int_{R_{ij}}^{\infty} \exp(-s_{ij} r) r^2 g_{ij}(r) dr \ . \tag{23}$$

Here $F_{1,r}^{*}$ describes repulsion of molecules, and $F_{1,a}^{*}$ describes their attraction.

Unlike the distribution function $g_{ij}(r)$, the Laplace transform of the product $r g_{ij}(r)$

$$G_{ij}(s) = 12(\eta_1 \eta_2)^{1/2} \int_{R_{ij}}^{\infty} \exp(-sr) r g_{ij}(r) dr \tag{24}$$

has been known in its analytical form and has simple enough functional form reported in [19]. According to the Laplace transform differentiation rule, we obtain

$$\frac{\partial G_{ij}(s)}{\partial s} \equiv G'_{ij}(s) = -12(\eta_1\eta_2)^{1/2} \int_{R_{ij}}^{\infty} \exp(-sr) r^2 g_{ij}(r) dr \,. \tag{25}$$

With allowance for Eq. (25), integrals (22) and (23) can be calculated analytically:

$$F^{r}_{1,ij} = -2\pi\rho\beta\varepsilon_{ij} e^{2s_{ij} r_{m,ij}} G'_{ij}(2s_{ij})\,, \tag{26}$$

$$F^{a}_{1,ij} = 4\pi\rho\beta\varepsilon_{ij} e^{s_{ij} r_{m,ij}} G'_{ij}(s_{ij})\,. \tag{27}$$

Let us consider the second term of the Helmholtz energy $F_{2,ij}$ described by formula (20). The integral entering into this equation is calculated numerically. It has finite integration limits from R_{ij} to λ_{ij}. It can be demonstrated that the ratio λ_{ij}/R_{ij} does not exceed 2. Therefore, to calculate integral (20), it is sufficient to know the distribution function $g_{ij}(r)$ only for $1 \le r/R_{ij} \le 2$. In this range, the function g_{ij} can be calculated fast and with high accuracy. It was established that the optimal number of points subdividing the integration interval in Eq. (20) that allowed $F_{2,ij}$ to be calculated with high accuracy (no worse than $1\cdot 10^{-8}$) was $N = 500$. Thus, the final formula for calculating the Helmholtz free energy of the binary mixture assumes the following form:

$$\frac{\beta F^{ex}}{N} = \frac{\beta F_{HS}}{N} + 2\pi\rho\beta \sum_{i,j=1}^{2} x_i x_j \left(-e^{2s_{ij} r^*_{ij}} \varepsilon_{ij} G'_{ij}(2s_{ij}) + 2e^{s_{ij} r^*_{ij}} \varepsilon_{ij} G'_{ij}(s_{ij}) - \int_{R_{ij}}^{\lambda_{ij}} \varphi^{\text{ref}}_{ij}(r) g_{ij}(r) r^2 dr\right). \tag{28}$$

The dimensionless pressure $Z = PV/NkBT$ is calculated by numerical differentiation of the Helmholtz excessive energy:

$$Z = 1 + \rho\beta(\partial F_{ex}/\partial\rho)_\beta\,. \tag{29}$$

The excessive internal energy per molecule is calculated analogously:

$$U_{ex} = (\partial(\beta F_{ex})/\partial\beta)_\rho\,. \tag{30}$$

Partial derivatives of the Helmholtz excessive energy with respect to variables ρ and β entering into Eqs. (29)–(30) are calculated by numerical differentiation of the function on a uniform grid with four neighboring nodes. For this purpose, the formula providing the fourth order of accuracy in the grid step was sufficient. This formula was derived by the Runge–Romberg method from the standard formula of numerical differentiation with respect to two nodes which has only the second order of accuracy.

SCHEMES OF POTENTIAL SUBDIVISION AND CALCULATED RESULTS

In this work, the thermodynamic parameters of the equimolar H and H_2 mixture was calculated using different potential subdivision schemes and compared with the results of modeling by the MC method. The data are presented here for three isotherms (10^3, $5\cdot 10^3$, and 10^4 K or for kT/ε_{22} = 49.5, 247.5 and 495.0) corresponding to temperature intervals at which the mixture of hydrogen atoms and molecules does exist. At temperatures below 10^3 K, hydrogen is in the molecular form, and at temperatures above 10^4 K, the thermal ionization causes a significant amount of atomic hydrogen to be formed. The calculated results and the MC data are tabulated in Tables 2–4. The first column of each table designated by MC gives values of the excessive pressure and internal energy calculated by the MC method.

TABLE 2. Calculated Thermodynamic Parameters of the H_2 + H Mixture at $T = 1000$ K

ρ	Parameters	MC	WCA	$N = 0$	$N = 1$	Eqs. (34) and (35)	Eqs. (34) and (36)
0.01	F		0.201	0.201	0.198	0.180	0.180
	Z	1.189	1.217	1.216	1.213	1.191	1.191
	U	0.0411	0.0445	0.0445	0.0418	0.0426	0.0426
0.033	F		0.796	0.796	0.782	0.687	0.687
	Z	1.855	2.005	1.999	1.982	1.825	1.825
	U	0.228	0.254	0.254	0.242	0.227	0.227
0.06	F		1.780	1.640	1.610	1.486	1.486
	Z	3.123	3.544	2.998	2.959	3.104	3.104
	U	0.675	0.782	0.661	0.631	0.676	0.676
0.1	F		3.747	3.275	3.265	3.216	3.236
	Z	6.002	6.403	6.475	6.368	5.914	6.065
	U	1.889	2.065	2.067	2.027	1.863	1.917
0.13	F		–	5.126	5.075	4.869	4.932
	Z	8.808	–	9.895	9.692	8.925	9.108
	U	3.216	–	3.673	3.582	3.264	3.339
0.2	F		–	10.885	10.709	10.019	10.186
	Z	16.986	–	19.964	19.589	18.056	18.371
	U	7.506	–	9.009	8.806	8.056	8.209

We also considered the case in which the WCA subdivision scheme was used for the three potentials without Eq. (12):

$$F_{ij}(r,\lambda_{ij}) = \varphi_{ij}(r_{ij}^{*}),$$

$$\lambda_{ij} = r_{ij}^{*}.$$

The corresponding values of $\beta F^{ex}/N$, $\beta U^{ex}/N$, and Z are given in the second columns of Tables 2–4 designated by WCA. In this case, they differ significantly from the MC data and increase for higher temperatures and densities. Moreover, no physically substantiated solution exists for high densities when the packing factor of the basic system is much greater than 0.5. We note that for the two-component mixture with

$$\eta = \frac{1}{6}\pi\rho(x_1 R_{11}^3 + x_2 R_{22}^3),$$

the hard-sphere packing factor η can exceed 0.5 or even 1.0 depending on the ratios ρ_1/ρ_2 and R_{11}/R_{22}, whereas the purely hard-sphere fluid is frozen at $\eta = 0.494$.

At the same time, the results obtained for the single-component fluids with high densities and temperatures based on the potential subdivision scheme suggested by Kang *et al.* [13]

$$F_{ij}(r,\lambda_{ij}) = \varphi_{ij}(\lambda_{ij}) + (r - \lambda_{ij})\varphi_{ij}'(\lambda_{ij}),$$
$$\lambda_{ij} = \min(a_{fcc}, r_{ij}^{*}), \tag{31}$$

TABLE 3. Calculated Thermodynamic Parameters of the H_2 + H Mixture at T = 5000 K

ρ	Parameters	MC	WCA	$N = 0$	$N = 1$	Eqs. (34) and (35)	Eqs. (34) and (36)
0.033	F		0.417	0.417	0.414	0.348	0.348
	Z	1.381	1.458	1.458	1.454	1.368	1.368
	U	0.176	0.197	0.197	0.194	0.175	0.175
0.05	F		0.665	0.649	0.645	0.543	0.543
	Z	1.623	1.759	1.681	1.675	1.592	1.592
	U	0.293	0.336	0.323	0.318	0.288	0.288
0.12	F		1.877	1.629	1.615	1.519	1.519
	Z	2.938	3.261	2.757	2.741	2.955	2.955
	U	0.987	1.139	0.939	0.926	1.001	1.001
0.17	F		2.833	2.416	2.415	2.406	2.411
	Z	4.138	4.251	4.331	4.299	4.049	4.173
	U	1.672	1.798	1.773	1.759	1.652	1.706
0.6	F		–	14.345	14.169	13.275	13.484
	Z	18.818	–	20.776	20.530	19.182	19.459
	U	11.54	–	13.245	13.029	12.034	12.248
1.0	F		–	28.481	28.166	26.385	26.776
	Z	35.31	–	38.168	37.873	35.713	36.159
	U	24.07	–	27.264	26.940	25.032	25.445

TABLE 4. Calculated Thermodynamic Parameters of the H_2 + H Mixture at T = 10000 K

ρ	Parameters	MC	WCA	$N = 0$	$N = 1$	Eqs. (34) and (35)	Eqs. (34) and (36)
0.033	F		0.295	0.295	0.293	0.240	0.240
	Z	1.252	1.313	1.312	1.310	1.246	1.246
	U	0.135	0.156	0.156	0.154	0.136	0.136
0.1	F		0.995	0.904	0.899	0.779	0.779
	Z	1.92	2.126	1.898	1.892	1.880	1.880
	U	0.516	0.608	0.529	0.524	0.502	0.502
0.2	F		2.164	1.828	1.815	1.791	1.791
	Z	3.212	3.337	2.922	2.909	3.278	3.278
	U	1.309	1.437	1.207	1.195	1.345	1.345
0.23	F		2.511	2.144	2.143	2.133	2.138
	Z	3.653	3.618	3.781	3.761	3.561	3.658
	U	1.59	1.675	1.664	1.654	1.568	1.609
0.4	F		–	4.449	4.422	4.244	4.298
	Z	6.465	–	6.919	6.843	6.418	6.516
	U	3.49	–	3.818	3.765	3.501	3.566
0.6	F		–	7.614	7.547	7.152	7.252
	Z	10.217	–	11.012	10.892	10.238	10.371
	U	6.202	–	6.883	6.780	6.286	6.396
1.0	F		–	14.736	14.596	13.781	13.963
	Z	18.24	–	19.673	19.509	18.508	18.698
	U	12.55	–	13.902	13.720	12.756	12.963

are in good agreement with the MC data. Therefore, it is reasonable to assume that this subdivision scheme will also work well for the two-component mixtures. The nonadditivity problem for hard-sphere diameters can be eliminated by choosing a proper subdivision scheme for the potential $\varphi_{12}(r)$. The schemes described below are applicable only to the cross potential $\varphi_{12}(r)$, whereas potential subdivision scheme (31) can also be used for the potentials $\varphi_{11}(r)$ and $\varphi_{22}(r)$.

The application of the polynomial subdivision scheme for the potential $\varphi_{12}(r)$ in the form

$$F_{12}(r,\lambda_{12}) = \sum_{n=0}^{N} \frac{(r-\lambda_{12})^n}{n!} \left.\frac{d^n\varphi_{12}}{dr^n}\right|_{r=\lambda_{12}} \tag{32}$$

provides the continuity of $\varphi_{12}^{\mathrm{pert}}(r)$ at $r = \lambda_{12}$. The resultant potential $\varphi_{12}^{\mathrm{ref}}(r)$ will be repulsive if

$$\lambda_{12} \le R_N ,$$

where R_N is determined from the formula

$$\left.\frac{d^{N+1}\varphi_{12}}{dr^{N+1}}\right|_{R_N} = 0 .$$

The subdivision point λ_{12} whose position depends on the temperature and density is chosen from the condition

$$I_{12}(\lambda_{12}) = 0 . \tag{33}$$

Polynomial potential subdivision scheme (32) is based on the Kahl–Hafner potential subdivision scheme [17] at $N = 0$ and schemes 1 and 4 with $N = 1$ and $N = 4$ suggested by Kang *et al.* [13].

It can be easily demonstrated that for polynomial potential subdivision scheme (32), the function $I_{12}(\lambda_{12})$ has a minimum at $\lambda_{12} = R_N$. Therefore, the value $\lambda_{12} = R_N$ must be chosen when Eq. (33) has no solution (for example, for a 1000 K isotherm and $\eta < 0.35$). Figure 1 illustrates the behavior of $I_{12}(\lambda_{12} = R_N)$ versus the density for a 1000 K isotherm with $N = 0$ and 1.

In the columns of Tables 2–4 designated by $N = 0$ and $N = 1$, the calculated Helmholtz energy, pressure, and internal energy are tabulated for $N = 0$ and 1, respectively. They are in satisfactory agreement with the MC data. For low densities when Eq. (33) has no solution, the differences increase with temperature. For high densities when the subdivision point λ_{12} can be calculated from Eq. (33), the data calculated using potential subdivision scheme (32) deviate considerably from the MC data. Hence the functional form of the smoothing potential $F_{12}(r, \lambda_{12})$ given by polynomial (32) is unsuitable for the examined ranges of density and temperature variations. With increasing N, the agreement with the MC data is slightly improved, but computations become more complicated. Therefore, the results calculated for $N > 4$ are not presented in this work. Unlike [14], the present work considers the potential subdivision with the use of polynomials of degree up to $N = 4$.

We used two forms of the smoothing potential $F_{12}(r, \lambda_{12})$ suggested in [14]. These potential subdivision schemes eliminate the nonadditivity problem for the reference potential, since condition (1) and Eqs. (12) hold true. This improves the agreement of the calculated thermodynamic parameters with the MC data in the entire range of density variations. To implement these subdivision schemes, three regions of density variations were first established in which different potential subdivision schemes were used. For region I, the isotherm was specified by the conditions $I_{12}(\lambda_{12} = R_0) > 0$ and $I_{12}(\lambda_{12} = R_1) > 0$. Region III was specified by the condition $I_{12}(\lambda_{12} = R_0) < 0$, and region II was intermediate between regions I and III. All three regions are shown in Fig. 1.

To satisfy condition (12) in region I, the form of the smoothing potential $F_{12}(r, \lambda_{12})$ must provide a significant increase in the repulsion potential $\varphi_{12}(r)$ in the vicinity of the hard-sphere diameter R_{12}. A hyperbolic cosine

$$F_{12}(r,\lambda_{12}) = \varphi_{12}(\lambda_{12}) + (r-\lambda_{12})\varphi_{12}'(\lambda_{12}) f(r,\lambda_{12})$$

is an example of this form. Here

$$f(r,\ \lambda_{12}) = 1 + A\left[1 - \frac{\cosh(r - R_{12})}{\cosh(\lambda_{12} - R_{12})}\right],$$
$$\lambda_{12} = R_1,\ A \ge 0. \tag{34}$$

The amplitude A of the hyperbolic cosine in region I can be found from Eq. (12). The form of expression (34) was chosen to reduce Eq. (34) to Eq. (32) for $N = 1$ (termination of region I of high densities). This provides the continuity of $\varphi_{12}^{\mathrm{pert}}(r)$ at $r = \lambda_{12}$. Since $A > 0$, the potential $\varphi_{12}^{\mathrm{ref}}(r)$ remains too repulsive; in region I, it satisfies the condition $I_{12} = 0$.

Tables 2–4 demonstrate that polynomial schemes (32) overestimate the internal energy and pressure in region III. This means that the potential $\varphi_{12}^{\mathrm{ref}}(r)$ remains too repulsive at these densities. For densities from region III, we can use the smoothing potential of the form

$$F_{12}(r,\lambda_{12}) = \varphi_{12}(\lambda_{12}) + \alpha[\varphi_{12}(r) - \varphi_{12}(\lambda_{12})],$$
$$\lambda_{12} = R_0 = r_{12}^{*},\ 0 \le \alpha < 1. \tag{35}$$

The parameter α is determined from Eq. (12) whose solution always exists.

For densities from region II, Eq. (32) with $N = 1$ was used to provide continuous transition from Eq. (34) to Eq. (35). The smoothing potentials calculated from Eqs. (34) and (35) are presented in columns 5 of Tables 2–4 and in Figs. 2 and 3. Closed circles show the results of modeling by the MC method, open triangles show the results of calculations using the polynomial with $N = 1$ for the smoothing cross potential, solid curves show the results of calculations by Eq. (34), dashed curves show the results of calculations by Eq. (35), and dash-dotted curves show the results of calculations by Eq. (36). Values of the pressure and internal energy calculated by Eqs. (34) and (35) agree very well with the MC data in the corresponding regions of density variations. However, it appears that Eq. (34) works better at low temperatures, whereas Eq. (35) slightly overestimates the pressure and internal energy under these conditions.

In spite of the fact that the free energy is a continuous function of the density and temperature, its first derivatives are not continuous functions. The presence of discontinuities in the thermodynamic functions on the interface between regions II and III worsens the agreement with the MC data.

To provide the continuity of the free energy when going from region II to region III, the slightly different form of $F_{12}(r, \lambda_{12})$:

$$F_{12}(r,\lambda_{12}) = \varphi_{12}(r),$$
$$\lambda_{12} = R_0 = r_{12}^{*},\ 0 \le s < s_{12}, \tag{36}$$

was used in region III. The hardness of the Morse potential s_{12} is the unknown parameter of this subdivision scheme. For $s = 0$, it is reduced to the WCA form. Results of calculations by Eqs. (34) and (36) are presented in columns 6 of Tables 2–4 and are shown by the dash-dotted curves in Figs. 2 and 3. The calculation errors are much smaller than those for polynomial potential subdivision schemes.

For high densities, the potential subdivision scheme based on Eq. (35) yields the best agreement of the calculated results with the MC data for each isotherm. Both forms of the smoothing potential significantly improve the agreement with the MC data compared to the polynomial forms of the smoothing potential. However, the schemes for the smoothing cross potential based on Eqs. (34)–(36) do not allow us to obtain complete agreement with the MC data. Probably, other potential subdivision schemes, for example, based on the application of two-parameter smoothing potentials must be used. In this case, numerical implementation of the method will be complicated significantly.

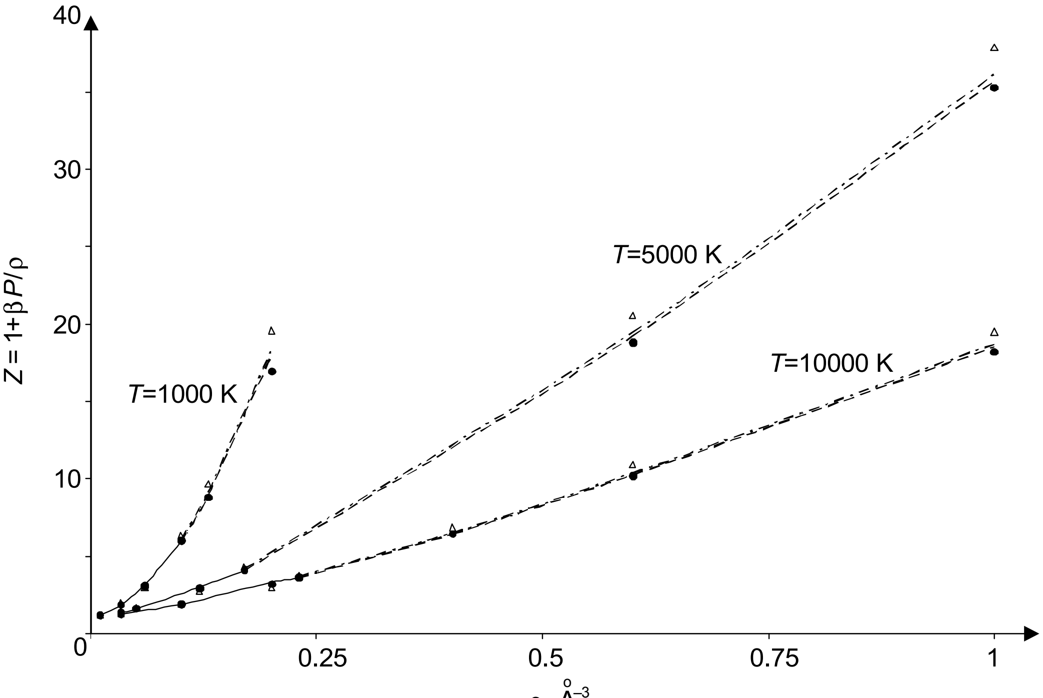

Fig. 2. Dependence of the dimensionless pressure on the density for different schemes of cross potential subdivision described in the text for the indicated isotherms.

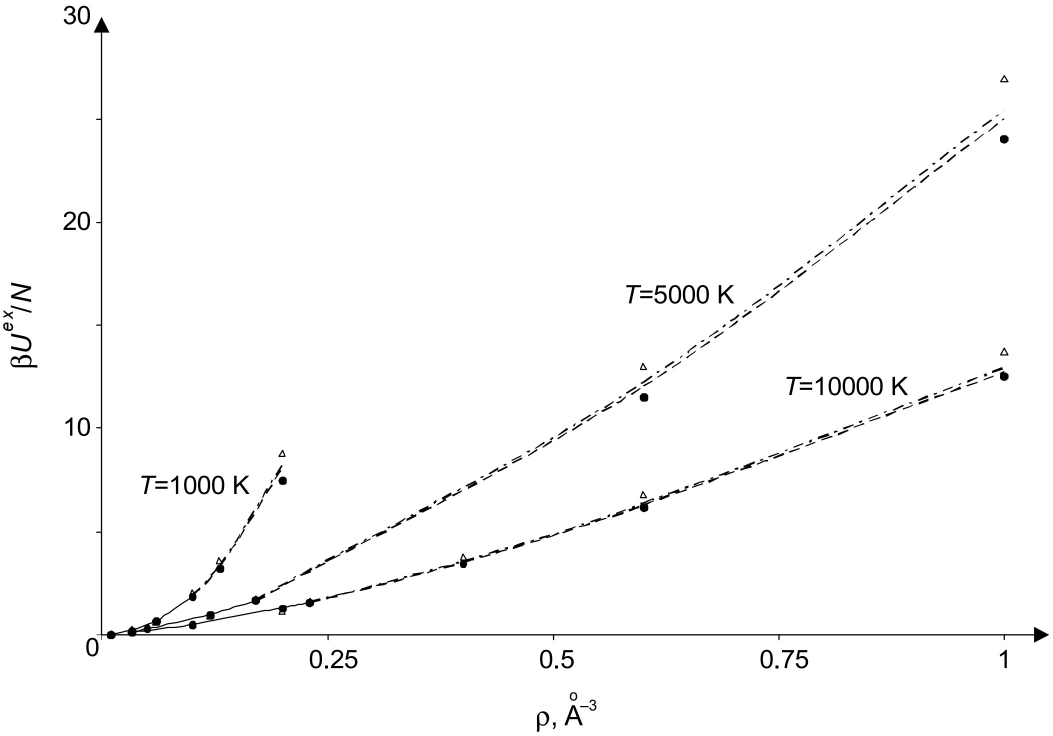

Fig. 3. Dependence of the excessive internal energy on the density for the cross-potential subdivision schemes described in the text for the indicated isotherms.

CONCLUSIONS

1. The algorithm of calculating the thermodynamic parameters of the two-component mixture of hydrogen atoms and molecules interacting with the Morse potential has been developed based on the perturbation theory.

2. It was demonstrated that the correct choice of the potential subdivision scheme reproduced exactly the thermodynamic properties of the two-component mixture at high temperatures and densities.

3. If the efficiency of the potential subdivision scheme is proved by the agreement of the calculated results with the MC data, this scheme becomes a very convenient computational tool that can be used to reproduce exactly the thermodynamic properties of the two-component mixture at high temperatures and densities.

4. The application of linear subdivision scheme (31) for the potentials $\varphi_{11}(r)$ and $\varphi_{22}(r)$ and Eq. (34) for the smoothing cross potential $F_{12}(r, \lambda_{12})$ for densities from region I (see Fig. 1) yields better agreement of the calculated pressure and internal energy with the MC data compared to the WCA scheme. For densities from region III where the WCA method yields only satisfactory or nonphysical results, application of Eq. (35) in the subdivision scheme for the potential $\varphi_{12}(r)$ yields good agreement with the MC data.

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