

A FIRST ORDER PERTURBATION THEORY OF SOLUTIONS

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A first order perturbation expansion is proposed using the Weeks-Chandler-Andersen choice of the reference system for solutions of non-electrolytes formed by molecules with central type of the interaction potential (involving soft repulsions). The Percus-Yevick approximation for a mixture of additive hard spheres is used in the calculation of the functions of the reference system. The method is applied to determine the excess thermodynamic functions ΔG^E , ΔH^E and ΔV^E of the argon-krypton system at $T = 115.8$ K and the krypton-xenon system at $T = 161.4$ K. The excess functions are compared with the Monte Carlo data and those following from the theory of Barker and Henderson and the variational approach due to Mansoori and Canfield.

Recently, the perturbation methods have been applied successfully to determine the state and thermodynamic behaviour of systems of non-electrolytes. A number of perturbation methods have been proposed (*e.g.* ref.^{1,2}) of which for pure substances in particular proved useful the approach of Barker and Henderson³, the Weeks-Chandler-Anderson⁴ (WCA) method and the Verlet-Weis⁵ method; the last being a modification of WCA method. Of these methods only the Barker-Henderson⁶ (BH) method and the Mansoori-Canfield⁷ (V) variational approach were extended to solutions. The Mansoori-Canfield method differs from BH in the way of determining the representative hard spheres and some mathematical details. In addition to the exact and versatile theories several approximative methods (*e.g.* the Snider-Herrington⁸ method) as well as those suitable for a certain type of intermolecular pair potential (Boublik-Benson⁹) have been proposed. These methods serve for their relative simplicity to estimate the thermodynamic functions of mixtures without, however, enabling exact study of multicomponent system with an arbitrary type of the intermolecular potential. WCA approach will be now extended to multicomponent systems since, as has been shown by Verlet and Weis⁵, WCA choice of the reference system, together with WCA approximation of the radial distribution function leads for the Lennard-Jones types of pair potential (involving soft repulsions) to so far the best agreement of the computed values with the pseudo-experimental Monte Carlo results.

THEORETICAL

A basic relation in statistico-thermodynamic description of the behaviour of mixtures by perturbation methods is the expression for the Helmholtz function. If the studied system contains N_A molecules type of A, N_B molecules of type B *etc.*, and a total

of N molecules ($N = N_A + N_B + \dots$) in a volume V at a temperature T , the first order perturbation expansion for the mixture takes the form

$$\frac{F}{NkT} = \frac{F^0}{NkT} + \frac{2\pi n}{kT} \sum_{i,j} x_i x_j \int w_{ij}(r) g_{ij}^0(r) r^2 dr; \quad (1)$$

where F and F^0 stand for the configuration free energy of the studied and the reference system respectively. k is the Boltzmann constant, $\beta = (kT)^{-1}$, n the number density ($n = N/V$), $x_i = N_i/N$ the mole fraction of the component i . $w_{ij}(r)$ and $g_{ij}^0(r)$ denote the perturbation interaction potential and the radial distribution function of the reference system respectively both for a pair of molecules of i and j type with the center-to-center distance equalling r . If $u_{ij}(r)$ is the pair potential of the studied system and $u_{ij}^0(r)$ and $w_{ij}(r)$ are the reference and the perturbation potentials respectively, then with WCA choice we have^{4,5}

$$u_{ij}^0(r) = u_{ij}(r) - u_{ij}(r_{ij}^*) \quad \text{for } r < r_{ij}^*; \quad u_{ij}^0(r) = 0, \quad r > r_{ij}^*; \quad (2a)$$

$$w_{ij}(r) = u_{ij}(r_{ij}^*), \quad r < r_{ij}^*; \quad w_{ij}(r) = u_{ij}(r), \quad r > r_{ij}^*. \quad (2b)$$

r_{ij}^* in the last equation stands for the intermolecular distance in the minimum of the potential curve where $u_{ij}(r_{ij}^*) = -\epsilon_{ij}$. For a reference system with a potential given by Eq. (2a) the course of the radial distribution function is not known, and, consequently, $g_{ij}^0(r)$ has to be expressed in an approximative manner. For pure substances it has proved useful to put $g^0(r) = \exp[-\beta u^0(r)] Y^{hs}(r)$. We shall therefore adopt for mixtures analogously the relation

$$g_{ij}^0(r) = \exp[-\beta u_{ij}^0(r)] Y_{ij}(r). \quad (3)$$

Function $Y_{ij}(r) \equiv Y_{ij}^{hs}(r)$ is given by

$$Y_{ij}(r) = \exp[\beta u_{ij}^{hs}(r)] g_{ij}^{hs}(r), \quad (4)$$

where the superscript hs indicates mixtures of hard spheres of diameter d_{ij} of the same composition $\{x_i\}$ as the studied and the reference system. Similarly as in the case of one-component system¹⁰ one can write for the free energy of the reference multicomponent system the functional Taylor expansion in terms of $\varphi_{ij}(r)$

$$\varphi_{ij}(r) = \exp[-\beta u_{ij}^0(r)], \quad (5)$$

about the potential of hard spheres, which for the $i - j$ type pair we shall designate

by $\varphi_{ij}^{hs}(r)$. With the aid of Eq. (3) one can derive for binary mixtures the relation

$$\begin{aligned} \frac{F^0}{VkT} = \frac{F^{hs}}{VkT} - \frac{1}{2} n_A^2 \int Y_{AA}(r) [\varphi_{AA}^0(r) - \varphi_{AA}^{hs}(r)] dr - \\ - n_A n_B \int Y_{AB}(r) [\varphi_{AB}^0(r) - \varphi_{AB}^{hs}(r)] dr - \frac{1}{2} n_B^2 \int Y_{BB}(r) [\varphi_{BB}^0(r) - \varphi_{BB}^{hs}(r)] dr + \dots, \end{aligned} \quad (6)$$

where the contribution of all terms higher than the first order is very small. If the thermodynamic functions for mixtures of "non-additive hard spheres" were known with sufficient accuracy, all three integrals in the last equation could be put equal zero. The free energy of the reference system would then equal — spare for higher order terms — the free energy of the mixture of hard spheres of the diameter given by the following equation

$$\int Y_{ij}(r) [\varphi_{ij}^0(r) - \varphi_{ij}^{hs}(r)] dr = 0 \quad (7)$$

for all possible types of pairs. Since, however, only the data on "additive hard spheres" are at our disposal, Eq. (7) can be used to determine only d_{ii} for which after some arrangement we get

$$\int_0^{r_{ii}^*} Y_{ii}(r) \exp[-\beta u_{ii}^0(r)] r^2 dr = \int_{d_{ii}}^{r_{ii}^*} Y_{ii}(r) r^2 dr. \quad (8)$$

The diameter of representative hard spheres of $i \neq j$ pairs is given by the arithmetic average

$$d_{ij} = (d_{ii} + d_{jj})/2. \quad (9)$$

In view of the definition of the reference system and the approximation in Eq. (3) it is convenient to split the integration interval in Eq. (1) into two parts: $(0 - r_{ij}^*)$ and $(r_{ij}^* - \infty)$

$$\begin{aligned} \frac{F}{NkT} = \frac{F^0}{NkT} + \frac{2\pi n}{kT} \sum_{i,j} x_i x_j \left\{ -\varepsilon_{ij} \int_0^{r_{ij}^*} Y_{ij}(r) \exp[-\beta u_{ij}^0(r)] r^2 dr + \right. \\ \left. + \int_{r_{ij}^*}^{\infty} w_{ij}(r) Y_{ij}(r) r^2 dr \right\}. \end{aligned} \quad (10)$$

The second integral may be expressed with the aid of the Laplace transforms of func-

tions $z g_{ij}^{hs}(z)$ (where $z = r/d_{ij}$; for $z > r_{ij}^*/d_{ij}$ $g_{ij}^{hs} = Y_{ij}$),

$$L\{z g_{ij}^{hs}(z)\} = G_{ij}(s), \quad (11)$$

and the inverse Laplace transforms of functions $z w_{ij}^*(z)$ (where $w_{ij}^*(r) = w_{ij}(r)/\epsilon_{ij}$)

$$L^{-1}\{z w_{ij}^*(z)\} = U_{ij}(s). \quad (12)$$

After substitution we get

$$\begin{aligned} \frac{F}{NkT} = \frac{F^0}{NkT} + \frac{2\pi n}{kT} \sum_{i,j} x_i x_j d_{ij}^3 \epsilon_{ij} \left\{ - \int_0^{r_{ij}^*/d_{ij}} Y_{ij}(z) \exp[-\beta u_{ij}^0(z)] z^2 dz + \right. \\ \left. + \int_0^\infty G_{ij}(s) U_{ij}(s) ds - \int_1^{r_{ij}^*/d_{ij}} u_{ij}^*(z) Y_{ij}(z) z^2 dz \right\}. \end{aligned} \quad (13)$$

This equation can be arranged using eq. (9) and (14)

$$u_{ij}^{0*}(z) = u_{ij}^0(z)/\epsilon_{ij} = u_{ij}^*(z) + 1, \quad (14)$$

to give

$$\frac{F}{NkT} = \frac{F^0}{NkT} + \frac{2\pi n}{kT} \sum_{i,j} x_i x_j d_{ij}^3 \epsilon_{ij} \left\{ \int_0^\infty G_{ij}(s) U_{ij}(s) ds - \int_1^{r_{ij}^*/d_{ij}} u_{ij}^{0*}(z) Y_{ij}(z) z^2 dz \right\} + \delta, \quad (15)$$

where

$$\delta = \frac{2\pi n}{kT} \sum_{i \neq j} x_i x_j d_{ij}^3 \epsilon_{ij} \left\{ \int_1^{r_{ij}^*/d_{ij}} Y_{ij}(z) z^2 dz - \int_0^{r_{ij}^*/d_{ij}} Y_{ij}(z) \exp[-\beta u_{ij}^0(z)] z^2 dz \right\}. \quad (16)$$

The free energy F^0 of the reference system can be expressed from Eq. (6) using expressions for a mixture of hard spheres

$$\frac{F^0}{NkT} = \frac{F^{hs}}{NkT} + 2\pi n \sum_{i \neq j} x_i x_j d_{ij}^3 \int_0^{r_{ij}^*/d_{ij}} Y_{ij}(z) [\varphi_{ij}^{hs}(z) - \varphi_{ij}^0(z)] z^2 dz. \quad (17)$$

Substituting the last expression into Eq. (15) we get

$$\begin{aligned} \frac{F}{NkT} = \frac{F^{hs}}{NkT} + \frac{2\pi n}{kT} \sum_{i,j} x_i x_j d_{ij}^3 \epsilon_{ij} \left\{ \int_0^\infty G_{ij}(s) U_{ij}(s) ds - \right. \\ \left. - \int_1^{r_{ij}^*/d_{ij}} u_{ij}^{0*}(z) Y_{ij}(z) z^2 dz \right\} + \Delta, \end{aligned} \quad (18)$$

where

$$\Delta = \frac{2\pi n}{kT} \sum_{i \neq j} x_i x_j d_{ij}^3 \epsilon_{ij} \left(1 + \frac{kT}{\epsilon_{ij}} \right) \int_0^{r_{ij}^*/d_{ij}} Y_{ij}(z) [\varphi_{ij}^{\text{hs}}(z) - \varphi_{ij}^0(z)] z^2 dz. \quad (19)$$

The function $Y_{ij}(r)$ for a system of hard spheres is a monotonically decreasing function on the interval $(0 - r_{ij}^*)$ with a maximum (a finite value) in the proximity of $r = 0$ (ref.¹¹). To calculate the integrals in Eq. (8) one can therefore approximate Y_{ij} by a first-order expansion in z at $z = 1$, i.e. we can write¹²

$$Y_{ij}(z) = A_{ij} + B_{ij}z, \quad (20)$$

where the coefficients A_{ij} and B_{ij} are determined from the value of the radial distribution function and the derivative of the expression for direct correlation function at the closest approach distance. The use of this approximation on the right hand side of Eq. (8) is justified by the narrowness of the integration interval; on the left hand side then by the properties of the factor $\exp[-\beta u_{ij}^0(r)]$ of Y_{ij} .

On substituting from Eq. (20) into (8) the parameters $c_{ii} = d_{ii}/\sigma_{ii}$ (where σ_{ii} is the characteristic length in the pair potential of a given component of the studied systems) can be easily determined from

$$A_{ii} \{ I_{ii}^{(2)} - \frac{1}{3} [(r_{ii}^*/\sigma_{ii})^3 - c_{ii}^3] \} + \frac{1}{c_{ii}} B_{ii} \{ I_{ii}^{(3)} - \frac{1}{4} [(r_{ii}^*/\sigma_{ii})^4 - c_{ii}^4] \} = 0, \quad (21)$$

where for $I_{ij}^{(k)}$ we have

$$I_{ij}^{(k)} = \int_0^{r_{ij}^*/d_{ij}} \exp[-\beta u_{ij}^0(t)] t^k dt, \quad k = 2, 3. \quad (22)$$

The approximate Eq. (20) may be used to determine the second integrals in Eq. (18) and the integrals in Eq. (19). If

$$J_{ij}^{(k)} = \int_1^{r_{ij}^*/d_{ij}} u_{ij}^{0*}(z) z^k dz, \quad (23)$$

then

$$\frac{F}{NkT} = \frac{F^{\text{hs}}}{NkT} + \frac{2\pi n}{kT} \sum_{i,j} x_i x_j d_{ij}^3 \epsilon_{ij} \left\{ \int_0^\infty G_{ij}(s) U_{ij}(s) ds - [A_{ij} J_{ij}^{(2)} + B_{ij} J_{ij}^{(3)}] \right\} + \Delta, \quad (24)$$

where

$$\Delta = -\frac{2\pi n}{kT} \sum_{i \neq j} x_i x_j d_{ij}^3 \varepsilon_{ij} \left(1 + \frac{kT}{\varepsilon_{ij}} \right) \frac{1}{c_{ij}^3} \left\{ A_{ij} \left[I_{ij}^{(2)} - \frac{1}{3} (r_{ij}^*/\sigma_{ij})^3 + \frac{c_{ij}^3}{3} \right] + \right. \\ \left. + \frac{1}{c_{ij}} B_{ij} \left[I_{ij}^{(3)} - \frac{1}{4} (r_{ij}^*/\sigma_{ij})^4 + \frac{c_{ij}^4}{4} \right] \right\}. \quad (25)$$

Comparing the expression in the outmost parentheses of Eq. (25) with Eq. (22) we find that if $\sigma_{ii} = \sigma_{jj}$ and $\varepsilon_{ii} = \varepsilon_{jj}$, Δ vanishes; for systems whose components do not differ appreciably in pair potentials Δ is very small.

Expression (24) for the configuration free energy of the studied system is relatively simple. Differentiating with respect to T or V to determine the internal energy or pressure, however, one has to take into account the dependence of the parameters c_{ij} (or d_{ij}) on temperature and density. For the compressibility factor we can then find

$$\frac{PV}{NkT} = \frac{P^{hs}V}{NkT} + \frac{2\pi n}{kT} \sum_{i,j} x_i x_j d_{ij}^3 \varepsilon_{ij} \left\{ \int_0^\infty G_{ij}(s) U_{ij}(s) ds - [A_{ij}J_{ij}^{(2)} + B_{ij}J_{ij}^{(3)}] \right\} - \\ - \frac{2\pi n}{kT} \sum_{i,j} x_i x_j d_{ij}^3 \varepsilon_{ij} V \frac{\partial}{\partial V} \left\{ \int_0^\infty G_{ij}(s) U_{ij}(s) ds - [A_{ij}J_{ij}^{(2)} + B_{ij}J_{ij}^{(3)}] \right\} - \\ - V \sum_i \left(\frac{\partial F/NkT}{\partial c_{ii}} \right) \left(\frac{\partial c_{ii}}{\partial V} \right) - V \frac{\partial \Delta}{\partial V}, \quad (26)$$

while for the free energy we get

$$\frac{U}{NkT} = \frac{2\pi n}{kT} \sum_{i,j} x_i x_j d_{ij}^3 \varepsilon_{ij} \left\{ \int_0^\infty G_{ij}(s) U_{ij}(s) ds - [A_{ij}J_{ij}^{(2)} + B_{ij}J_{ij}^{(3)}] \right\} - \\ - T \sum_i \left(\frac{\partial F/NkT}{\partial c_{ii}} \right) \left(\frac{\partial c_{ii}}{\partial T} \right) - T \frac{\partial \Delta}{\partial T}. \quad (27)$$

RESULTS AND DISCUSSION

The proposed equations were used to calculate the excess thermodynamic functions at constant temperature and pressure $P \rightarrow 0$ of binary mixtures of the components whose molecules interact according to the Lennard-Jones 12-6 potential

$$u_{ij}(r) = 4\varepsilon_{ij} \left[(\sigma_{ij}/r)^{12} - (\sigma_{ij}/r)^6 \right], \quad (28)$$

assuming the Berthelot-Lorentz rule for determining the crossed characteristic para-

meters, *i.e.*

$$\varepsilon_{ij} = (\varepsilon_{ii}\varepsilon_{jj})^{1/2}, \quad \sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2. \quad (29)$$

The expressions, found for the Percus–Yevick approximation by Lebowitz¹³ and rearranged by Mansoori and Canfield⁷ to the form

$$G_{11}(s) = s\{H - L_2(s) \exp [s/\mu]\}/12 y_1 D(s), \quad (30)$$

$$G_{22}(s) = s\{H - L_1(s\mu) \exp [s\mu]\}/12 y_2 D(s\mu), \quad (31)$$

$$G_{12}(s) = v^4 s^2 \exp [s] \left\{ \left[\frac{3}{4} (y_2 - y_1) \left(\frac{1}{\mu} - 1 \right) v - \left(1 + \frac{\xi}{2} \right) s - (1 + 2\xi) \right] / D(vs) \right\}. \quad (32)$$

were used for the Laplace transform of $z g_{ij}^{hs}(z)$. Some quantities appearing in Eqs (30)–(32) are given as follows

$$y_i = \pi x_i N d_{ii}^3 / 6V, \quad i = 1, 2 \quad (33a)$$

$$y_{12} = \pi x_1 x_2 N d_{12}^3 / 3V, \quad (33b)$$

$$\mu = d_{11} / d_{22}, \quad (34a)$$

$$v = d_{11} / d_{12} = 2 \left(1 + \frac{1}{\mu} \right)^{-1}, \quad (34b)$$

$$\xi = y_1 + y_2, \quad (35)$$

$$H = 36 y_1 y_2 \mu (1 - \mu)^2, \quad (36)$$

$$L_1(t) = 12 y_2 A_1 t^2 + [12 y_2 \mu^3 (1 + 2\xi) - H] t + H, \quad (37)$$

$$L_2(t) = 12 y_1 A_2 t^2 + \left[12 y_1 (1 + 2\xi) - \frac{1}{\mu} H \right] t + H, \quad (38)$$

$$S(t) = H + A_3 t - 18 (y_1 + \mu y_2)^2 t^2 - 6 (y_1 + \mu y_2) (1 - \xi) t^3 - (1 - \xi)^2 t^4, \quad (39)$$

$$D(t) = H - L_1(t) \exp [t] - L_2(t) \exp [t/\mu] + S(t) \exp [t(1 + 1/\mu)], \quad (40)$$

$$A_1 = \mu^2 \left[\left(1 + \frac{\xi}{2} \right) + \frac{3}{2} y_1 \left(\frac{1}{\mu} - 1 \right) \right], \quad (41)$$

$$A_2 = \left[\left(1 + \frac{\xi}{2} \right) + \frac{3}{2} y_2 (\mu - 1) \right], \quad (42)$$

$$A_3 = 12(y_1 + \mu^3 y_2) (1 + 2\xi) - H \left(1 + \frac{1}{\mu} \right). \quad (43)$$

Eqs (30)–(32) together with

$$U_{ij}(s) = 4 [c_{ij}^{-12} s^{10} / 10! - c_{ij}^{-6} s^4 / 4!], \quad (44)$$

permit the first integrals in Eq. (24) to be determined by numerical integration. The compressibility factor of a mixture of hard spheres, $P^{hs}V/NkT$, was computed from¹⁴

$$P^{hs}V/NkT = (1 - \xi)^{-1} + 3\xi_1\xi_2/\xi_0(1 - \xi)^2 + (3 - \xi)\xi_2^3/\xi_0(1 - \xi)^3. \quad (45)$$

For the difference of the free energy of a mixture of hard spheres and that of an ideal gas mixture of the same composition, temperature and volume it follows

$$F^{hs}/NkT = (1 - \xi_2^3/\xi_0\xi^2) \ln [V/(V - \xi)] + (\xi_2^3 + 3\xi_1\xi_2\xi)/\xi_0\xi(1 - \xi) + \xi_2^3/\xi_0(1 - \xi)^2, \quad (46)$$

where

$$\xi_j = \pi N \sum_i x_i d_{ij}^3 / 6V \quad (47a)$$

and

$$\xi = \xi_3. \quad (47b)$$

The values of the radial distribution function $g_{ij}(1)$ were used together with the derivative (with respect to the distance) of the Percus Yevick-relation for the direct correlation function¹³ to determine A_{ij} and B_{ij}

$$Y_{ij}(1) = A_{ij} + B_{ij} = 1/(1 - \xi) + 3\xi_2 R_{ij} / 2(1 - \xi)^2 + \xi_2^2 R_{ij}^2 / 2(1 - \xi)^3, \quad (48)$$

$$Y'_{ij}(1) = B_{ij} = b_{ij} + 3e_{ij} R_{ij}^2, \quad (49)$$

where

$$R_{ij} = 2d_{ii}d_{jj}/(d_{ii} + d_{jj}), \quad (50)$$

$$e_{ij} = e(d_{ii} + d_{jj})/2, \quad (51)$$

$$e = \xi_0/2(1 - \xi)^2 + 3\xi_1\xi_2/(1 - \xi)^3 + 9\xi_2^3/2(1 - \xi)^4; \quad (52)$$

For b_{ij} we then have

$$b_{11} = -6[y_1g_{11}^2(1) + \frac{1}{4}\mu y_2(\mu + 1)^2 g_{12}^2(1)], \quad (53a)$$

$$b_{22} = -6\left[y_2g_{22}^2(1) + \frac{1}{4\mu} y_1(1 + 1/\mu)^2 g_{12}^2(1)\right], \quad (53b)$$

$$b_{12} = -6\left[\frac{1}{\mu} y_1g_{11}(1) + \mu y_2g_{22}(1)\right]g_{12}(1), \quad (53c)$$

$$g_{11}(1) = \{(1 + \xi/2) + 3y_2(\mu - 1)/2\}/(1 - \xi)^2, \quad (54a)$$

$$g_{22}(1) = \{(1 + \xi/2) + 3y_1(1/\mu - 1)/2\}/(1 - \xi)^2, \quad (54b)$$

$$g_{12}(1) = [d_{22}g_{11}(1) + d_{11}g_{22}(1)]/2d_{12}. \quad (54c)$$

For one-component system ($d = d_{ii}$ and $y = y_1 + y_2$) Eqs (48) and (49) simplify to (compare cit.¹²) the following relations

$$A = (1 + 4y + \frac{9}{2}y^2)/(1 - y)^3, \quad (55)$$

$$B = -9y(1 + y)/2(1 - y)^3, \quad (56)$$

used to determine the properties of pure components.

In the calculation of the excess thermodynamic functions we determined first the parameter c_{ii} and the volume V_i from Eqs (55) and (56) for a given temperature and pressure $P \rightarrow 0$. Having found the volumes and the diameter of the representative hard spheres $d_{ii} = c_{ii}\sigma_{ii}$ the free and the internal energy of pure components were computed.

In the calculation of the thermodynamic function for mixtures we used the above values of c_{ii} for pure components as it turned out that the change of c_{ii} corresponding to the change of the density from a pure component to the mixture for examined systems was negligible and the computer costs were considerably reduced. The mixed parameter c_{12} was determined from

$$c_{12} = (d_{11} + d_{22})/(\sigma_{11} + \sigma_{22}) \quad (57)$$

following from combining Eqs (19) and (29). From these parameters the volume of the mixture, V_s , at a given temperature and pressure $P \rightarrow 0$ was determined in an iterative manner. For the found volume V_s we then determined the values of the free energy and the Helmholtz function of the mixture under the given conditions as well as the excess free enthalpy, ΔG^E , the excess enthalpy, ΔH^E , and the excess volume, ΔV^E .

Table I gives a comparison of the excess functions for the argon-krypton system at $T = 115.8^\circ\text{K}$ ($P \rightarrow 0$) with the Monte Carlo data, found by McDonald¹⁵ by simulating in NPT ensemble (designated in the table as MC(a)), with the data of Singers¹⁶, obtained by simulation in NVT ensemble (designated as MC(b)), and with the values from the Barker-Henderson first order theory⁶ and the variational approach of Man-

TABLE I
A Comparison of the Excess Functions ΔG^E , ΔH^E and ΔV^E for the Argon-Krypton System at $T = 115.8\text{ K}$ and $P \rightarrow 0$ with the Monte Carlo (MC) Data, Results of the Barker-Henderson Theory (BH) and those of the Variational Approach of Mansoori and Canfield (V): ($\epsilon_{11}/k = 119.8\text{ K}$, $\epsilon_{22}/k = 167.0\text{ K}$, $\sigma_{11} = 3.405\text{ \AA}$, $\sigma_{22} = 3.633\text{ \AA}$)

x_1	This work	BH	V	MC(a)	MC(b)	Exp. ^{7,16}
$\Delta G^E, \text{ J/mol}$						
0.25	21	—	—	33	—	—
0.398	27	—	43	44	—	80
0.5	28	28	47	46	45	84
0.602	27	—	46	45	—	82
0.75	21	—	—	36	—	—
$\Delta H^E, \text{ J/mol}$						
0.25	— 3	—	—	—16	—	—
0.398	— 7	—	—	—24	—	—
0.5	—10	—54	—33.5	—29	—18	83
0.602	—12	—	—	—30	—	—
0.75	—12	—	—	—22	—	—
$\Delta V^E, \text{ ml/mol}$						
0.25	—0.29	—	—	—0.44	—	—
0.398	—0.41	—	—0.66	—0.61	—	—0.46
0.5	—0.46	—0.72	—0.73	—0.69	—0.60	—0.52
0.602	—0.48	—	—0.72	—0.69	—	—0.53
0.75	—0.42	—	—	—0.59	—	—

TABLE II

A Comparison of the Thermodynamic Properties of Argon, Krypton and their Equimolar Mixture at $T = 115.8$ K and $P \rightarrow 0$ with the Monte Carlo Data (MC), the Results of the Variational Approach of Mansoori and Canfield (V) and the Experimental Results

System	V , ml/mol this work	V	MC	Exp. ^{7,16}	$-H$, J/mol this work	V	MC	Exp. ^{7,16}
Ar	32.18	34.77	33.52	33.47	5 069	4 706	4 945	4 937
Kr	33.72	35.16	34.09	34.22	8 508	8 211	8 523	8 211
Ar + Kr	32.48	34.23	33.01	33.35	6 798	6 489	6 811	—

TABLE III

A Comparison of Computed Excess Functions ΔG^E , ΔH^E and ΔV^E for Equimolar Mixture of Argon and Xenon at $T = 161.4$ K and $P \rightarrow 0$ with the Monte Carlo (MC) Data and the Experimental Data ($\epsilon_{11}/k = 167.0$ K, $\epsilon_{22}/k = 229.9$ K, $\sigma_{11} = 3.633$ Å, $\sigma_{22} = 4.974$ Å)

Function	This work	MC	Exp. ^{7,16}
ΔG^E , J/mol	12.2	28.2	115.4
ΔH^E , J/mol	-39.4	-52.3	—
ΔV^E , ml/mol	-0.47	-0.70	-0.62

soori and Canfield^{7,16}. From comparison it follows that the results of the excess volume obtained in this work are somewhat lower than those of Barker and Henderson and the results of the variational approach. They are, however, in good agreement with the data of Singers; the agreement with the data of McDonald is somewhat worse. Lower values of ΔV^E cause probably the values of other two excess functions to decrease. The values of the excess free enthalpy, similarly as BH data, are lower than those of the Monte Carlo method. The variational approach (using the variation of F to determine the representative hard spheres) gives the best agreement for ΔG^E . The computed excess enthalpies are small in absolute values and in good agreement with MC(b) data. The deviations of the Barker-Henderson values, as well as those following from the variational approach, are considerable. Summarily, the discussed method and the variational approach, predict the excess functions with approximately same deviation; BH method is somewhat worse. Comparing, however, the total functions V , H instead of the excess values, as has been done in Table II

for argon, krypton and their equimolar mixture, the proposed method provides much better prediction than the variational approach.

Table III shows a comparison of the excess functions for an equimolar mixture of krypton and xenon at $T = 161.4$ K and $P \rightarrow 0$ with the Monte Carlo data¹⁶. The agreement can be considered as very good.

Tables I–III summarize also the experimental values of the function considered. A comparison of the computed values with the experimental data indicates also the proposed method to be superior over the variational approach and the Barker–Henderson method. This comparison is of course only a guide owing to the used characteristic parameters of the model potential.

It may be concluded that the perturbation expansion of the first order utilizing WCA choice of the reference system and WCA approximation of the radial distribution function represents a useful tool for description of multicomponent systems.

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Note added in proof: Recently, Barker and Henderson [*Mol. Phys.* **25**, 883 (1973)] published the recalculated data of the excess thermodynamic functions for the system argon–krypton at 115.8 K which are in very good agreement with the „pseudoexperimental“ data.