

A SECOND ORDER PERTURBATION THEORY FOR SYSTEMS WITH "SOFT" INTERMOLECULAR REPULSIONS

T. BOUBLÍK

*Institute of Chemical Process Fundamentals,
Czechoslovak Academy of Sciences, 165 02 Prague - Suchbát*

Received February 16th, 1973

A simple second-order perturbation expansion is proposed for systems consisting of simple spherical molecules with pair interaction potential involving a soft repulsion term utilizing the Weeks-Chandler-Andersen (WCA) choice of the reference system. The second-order perturbation term is approximated by the Barker-Henderson (m.c.) expression. The relations are formulated for the compressibility factor, internal energy and the Helmholtz function and further used to determine the thermodynamic functions of argon (for the Lennard-Jones 12-6 potential) at the reduced temperature 0.75, 1.15, 1.35 and 2.74 and the reduced density ranging between 0-1.0. The computed values were compared with the Monte-Carlo data and those following from WCA first-order theory.

A basic idea of perturbation theories, representing at present a most advanced method of statistico-thermodynamic description of state and thermodynamic behaviour of fluids, rests in expressing the potential energy of the studied system as a combination of the potential energy of the reference system plus the perturbation energy. The latter is substantially smaller than the former.

Of a number of perturbation theories, summarized *e.g.* in cit.^{1,2}, pertaining to fluids consisting of simple spherical molecules appears best the Barker-Henderson second-order³ expansion and the approach of Weeks, Chandler and Andersen^{4,5}. Barker and Henderson have found by studying a system of particles interacting according to the square-well model potential that the first order expansion is insufficient to describe the behaviour of fluids in liquid region. Expressing the energy of the system as a function of the number of pairs of molecules with a certain distance the authors have succeeded to approximate the second order perturbation term by the so-called m.c. (macroscopic compressibility), or l.c. (local compressibility), expressions of which the first appears somewhat simpler. The computations have shown the second-order perturbation expansion to give a better fit of the theoretical and pseudo-experimental data than the first-order one. The differences when using either m.c. or l.c. approximations are insignificant. Later, Smith, Barker and Henderson⁶ determined the second order term by superposition approximation. They obtained considerably more complex expression, which, moreover, did not yield a substantial improvement of the fit of the thermodynamic functions. When using the perturbation theory for systems with "soft" repulsions, where the pair interactions are given *e.g.* by the Lennard-Jones 12-6 potential (LJ 12-6), Barker and Henderson assumed the repulsions to be described by this potential in the range $r < \sigma$ (where σ is a characteristic length); the attractive forces were expressed by the same potential in the range $r > \sigma$. The mentioned division and the corresponding

choice of the reference system lead to a more slowly converging expansion than that in the case of the reference system according to Weeks, Chandler and Andersen^{4,5} (WCA). The latter authors assumed the whole part of the potential curve to the left of the potential minimum to correspond to repulsion and for the pair potential of the system they took LJ 12-6 potential increased by a value of the energy of the minimum (for $r < 2^{1/6}\sigma$). Verlet's calculations⁷ for LJ 12-6 have shown an excellent agreement of the theoretical values with the Monte Carlo results mainly at high densities. For the square well potential, however, the WCA relations change into the first order expansion investigated by Barker and Henderson. Recently, Alder Young and Mark have studied a system with the square well potential by the molecular dynamics⁸ and confirmed clearly that the second-order term in the perturbation expansion is important while the contribution of all higher-order terms is negligible. At the same time they conclude that the Barker-Henderson approximative expression for the given potential yields a good agreement with the Monte Carlo results.

In this paper a second-order perturbation expansion is proposed for WCA choice of the reference system.

In the proposed approach the radial distribution function of the hard spheres is approximated by a straight line in the neighbourhood of the closest approach distance. This approximation permits an easy determination of the diameter of the representative hard spheres to be made.

THEORETICAL

For a one-component system formed by N spheres in a volume V at a temperature T the perturbation expansion of the second order takes the form⁹

$$\beta F = \beta F_0 + \beta Q_1 - (\beta^2/2) Q_2, \quad (1)$$

where F and F_0 are the configuration free energy of the studied and the reference system, resp., $\beta = (kT)^{-1}$, k is the Boltzmann constant and Q_1 , Q_2 are the first- and second order perturbation terms. The first of these terms may be expressed on the basis of the distribution function $g_0(r)$ of the reference system

$$Q_1 = 2\pi Nn \int_0^\infty u_p(r) g_0(r) r^2 dr, \quad (2)$$

where r is the distance of the interacting particles, $u_p(r)$ is the perturbation pair potential and $n = N/V$ is the particle density. For the second order perturbation terms Barker and Henderson have found the following approximative formulas

$$Q_2(\text{m.c.}) = 2\pi Nn kT (\partial n / \partial P)_0 \int_0^\infty u_p^2(r) g_0(r) r^2 dr, \quad (3a)$$

or

$$Q_2(\text{l.c.}) = 2\pi N n k T \left(\frac{\partial n}{\partial P} \right)_0 \frac{\partial}{\partial n} n \int_0^\infty u_p^2(r) g_0(r) r^2 dr. \quad (3b)$$

The expressions in the perturbation expansion (1) were determined without prior specification of the reference system; one may thus choose WCA. If $u(r)$ is the pair potential of the studied system then for the pair potential of the reference system, $u_0(r)$, we have

$$\begin{aligned} u_0(r) &= u(r) - u(r_m), \quad \text{for } r < r_m; \\ u_0(r) &= 0, \quad r > r_m, \end{aligned} \quad (4)$$

(where r_m is the distance of the pairs of molecules corresponding to the minimum of the potential energy and $u(r_m) = -\varepsilon$). The perturbation potential is given by

$$u_p(r) = u(r_m), \quad \text{for } r < r_m; \quad u_p(r) = u(r), \quad \text{for } r > r_m. \quad (5)$$

The choice of the reference system is associated also with the approximation of the distribution function. For the above reference pair potential it proves useful to assume that

$$g_0(r) = \exp[-\beta u_0(r)] Y_h(r/d_h); \quad Y(r) = \exp[\beta u(r)] g(r). \quad (6), (7)$$

Subscript h indicates the function of a system of hard spheres of diameter d_h . This diameter is chosen so as to satisfy

$$4\pi \int \{Y_h \exp[-\beta u_0] - 1\} r^2 dr = 4\pi \int \{Y_h \exp[-\beta u_h] - 1\} r^2 dr. \quad (8)$$

Determining the hard sphere diameter in this way allows then the free energy of the reference system to be calculated easily because F_0 is given very precisely by the function F_h for hard spheres of the diameter d_h from Eq. (8)^{4,5}.

The last relation may be alternatively written, considering Eqs (4) and (5), as

$$\int_0^{r_m} Y_h \exp[-\beta u_0] r^2 dr = \int_{d_h}^{r_m} Y_h r^2 dr, \quad (9)$$

which considerably simplifies evaluation of the integrals in Eqs (2) and (3) in region $(0 - r_m)$, where the perturbation potential has a constant value $u(r_m)$. For the first

order perturbation term one may then write

$$Q_1 = 2\pi Nn \left\{ u(r_m) \int_{d_h}^{r_m} Y_h r^2 dr + \int_{r_m}^{\infty} Y_h u(r) r^2 dr \right\} = \\ = 2\pi Nn \left\{ u(r_m) \int_{d_h}^{r_m} Y_h r^2 dr + \int_{d_h}^{\infty} Y_h u(r) r^2 dr - \int_{d_h}^{r_m} Y_h u(r) r^2 dr \right\}. \quad (10)$$

The first and the third term of the last equation may be combined to give a single integral, see Eq. (4). The function Y_h in the second term equals the radial distribution function $g_h(r)$ in the whole range $r \geq d_h$. For the Percus-Yevick (PY) approximation of the radial distribution function the second integral may then be determined by means of the Laplace transform¹⁰ of the function $xg(x)$ (where $x = r/d_h$), which shall be denoted as $G(s) = L\{xg(x)\}$. If $u^*(x)$ is the pair potential of the studied system divided by ϵ , and $U_1(s)$ is the inverse Laplace transform of $xu^*(x)$ then for βQ_1 we have

$$\frac{\beta Q_1}{N} = \frac{2\pi n d_h^3}{kT} \left\{ \epsilon \int_0^{\infty} G(s) U_1(s) ds - \int_1^{r_m/d_h} u_0(x) Y_h(x) x^2 dx \right\} = \\ = \frac{12y}{T^*} \left\{ \int_0^{\infty} G(s) U_1(s) ds - \int_1^{r_m/d_h} u_0^*(x) Y_h(x) x^2 dx \right\}. \quad (11)$$

In the last equation $y = \pi n d_h^3/6$, the reduced temperature is defined as $T^* = kT/\epsilon$ and $u_0^*(x) = u_0(x)/\epsilon$.

In a similar way one may arrange also the second-order perturbation term: If $U_2(s)$ is the inverse Laplace transform of the function $x u^{*2}(x)^2$ we have

$$\frac{\beta^2 Q_2}{N} = \frac{2\pi n d_h^3 \epsilon^2}{(kT)^2} kT \left(\frac{\partial n}{\partial P} \right)_0 \left\{ \int_0^{\infty} G(s) U_2(s) ds - \int_1^{r_m/d_h} Y_h(x) [u^{*2}(x) - 1] x^2 dx \right\} = \\ = \frac{12y}{T^{*2}} \frac{1}{\beta(\partial P/\partial n)_0} \left\{ \int_0^{\infty} G(s) U_2(s) ds - \int_1^{r_m/d_h} Y_h(x) [u^{*2}(x) - 1] x^2 dx \right\}, \quad (12)$$

where unity in the second term corresponds to the value $u^2(r_m)/\epsilon^2$. The factor $kT(\partial n/\partial P)_0$ for the reference system may be again approximated by the function for a system of hard spheres of diameter d_h from Eq. (9).

With regard to the properties of the function $\exp[-\beta u_0(r)]$ the integrand $Y_h \exp[-\beta u_0]$ takes non-vanishing values only for distances differing little from r_m . The function Y_h may therefore be expressed in this narrow interval by the following linear relation

$$Y_h(x) = A + Bx, \quad (13)$$

where the parameters A and B are determined by the value of function g and its first derivative with respect to x in the point of contact ($x = 1$).

Denoting the ratio d_h/σ by c , where σ is the characteristic dimension of the pair potential $u(r)$, one may then obtain from Eq. (9) an expression

$$A\{I_2 - \frac{1}{3}[(r_m/\sigma)^3 - c^3]\} + \frac{B}{c}\{I_3 - \frac{1}{4}[(r_m/\sigma)^4 - c^4]\} = 0, \quad (14)$$

providing for a relatively easy determination of c and hence d_h for the studied pair potential. The integrals I_j in Eq. (14) depend only on the form of the potential function and the temperature

$$I_j = \int_0^{r_m/\sigma} \exp[-\beta u_0(z)] z^j dz, \quad z = r/\sigma. \quad (15)$$

Since the integration limits of the second integrals in Eqs (11) and (12) delimit a very narrow interval, one may also utilize the approximation expressed in Eq. (13) to evaluate Y_h analytically. Substituting for Q_1 and Q_2 in Eq. (1) we get

$$\begin{aligned} \frac{F}{NkT} = \frac{F_0}{NkT} + \frac{12y}{T^*} \left\{ \int_0^\infty G(s) U_1(s) ds - [AJ_2 + BJ_3] \right\} - \\ - \frac{6y}{T^{*2}} \frac{1}{\beta(\partial P/\partial n)_0} \left\{ \int_0^\infty G(s) U_2(s) ds - [AK_2 + BK_3] \right\}, \end{aligned} \quad (16)$$

where

$$J_j = \int_1^{r_m/d_h} u_0^*(x) x^j dx, \quad K_j = \int_1^{r_m/d_h} [u^{*2}(x) - 1] x^j dx, \quad \text{for } j = 2, 3. \quad (17a,b)$$

For the compressibility factor of the studied system we have

$$\begin{aligned} \frac{PV}{NkT} = f \left\{ \frac{P_0V}{NkT} + \frac{12y}{T^*} \int_0^\infty H(s) U_1(s) ds - \right. \\ \left. - \frac{6y}{T^{*2}} \left[\left(\frac{1}{\beta(\partial P/\partial n)} \right)' y \int_0^\infty G(s) U_2(s) ds - \frac{1}{\beta(\partial P/\partial n)} \int_0^\infty H(s) U_2(s) ds \right] \right\} + \\ + \frac{12y}{T^*} \int_0^\infty \left(\frac{\partial c}{\partial n} \right) \left(\frac{\partial U_1}{\partial c} \right) G(s) ds - \frac{6y}{T^{*2}} \frac{1}{\beta(\partial P/\partial n)} \int_0^\infty \left(\frac{\partial c}{\partial n} \right) \left(\frac{\partial U_2}{\partial c} \right) G(s) ds + \\ + n \frac{\partial}{\partial n} \left\{ - \frac{12y}{T^*} [AJ_2 + BJ_3] - \frac{6y}{T^{*2} \beta(\partial P/\partial n)} [AK_2 + BK_3] \right\}, \end{aligned} \quad (18)$$

where the second term in the factor $f = 1 + 3(n/c)(\partial c/\partial n)$ is usually negligible. $[1/\beta(\partial P/\partial n)]'$ denotes derivative with respect to y and the function $H(s)$ is given by the derivative $\partial yG/\partial y$.

For the internal energy U it follows from Eq. (16):

$$\begin{aligned} \frac{U}{NkT} = & \frac{12y}{T^*} \left\{ \int_0^\infty G(s) U_1(s) ds - [AJ_2 + BJ_3] \right\} - \\ & - \frac{12y}{T^{*2}\beta(\partial P/\partial n)} \left\{ \int_0^\infty G(s) U_2(s) ds - [AK_2 + BK_3] \right\} - T^* \frac{\partial(F/NkT)}{\partial c} \frac{\partial c}{\partial T^*}, \end{aligned} \quad (19)$$

where the last term appears as a consequence of the fact that the diameter of the hard spheres depends on temperature.

RESULTS AND DISCUSSION

Throughout this work we have adopted the Lennard-Jones potential. The reason for this choice was that LJ 12-6 system is the best known of those involving soft repulsions. Moreover, numerous pseudo-experimental data for a number of temperatures and densities are available for this system. The equations for the reference and perturbation pair potentials then take the form

$$u_0(r) = \varepsilon[2(\sigma/r)^6 - 1]^2 \quad \text{for } r < r_m; \quad u_0(r) = 0, \quad r > r_m, \quad (20a)$$

and

$$u_p(r) = -\varepsilon, \quad r < r_m; \quad u_p(r) = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6], \quad r < r_m, \quad (20b)$$

where $r_m = 2^{1/6}\sigma$.

For a system of hard spheres we have made use of the Carnahan Starling¹¹ equation of state

$$PV/NkT = (1 + y + y^2 - y^3)/(1 - y)^3. \quad (21)$$

The values of the radial distribution function at the closest approach distance following from this equation were used jointly with the derivative of PY approximation of the direct correlation function in the point $x = 1$ to determine the coefficients in Eq. (13). For A and B we thus get

$$A = (1 + 4y + 9y^2/2)/(1 - y)^3, \quad B = -9y(1 + y)/2(1 - y)^3. \quad (22), (23)$$

TABLE I

A Comparison of the Compressibility Factor (z), the Free Energy (F) and the Internal Energy (U) of a System of LJ 12-6 Particles Computed from the Second-Order Perturbation Theory with those from the Verlet-Weis First-Order Theory and the Monte Carlo Data

$\rho\sigma^3$	2nd order			1st order			MC		
	z	F/NkT	$U/N\epsilon$	z	F/NkT	$U/N\epsilon$	z	F/NkT	$U/N\epsilon$
$T^* = 0.75$									
0.1	0.31	-0.72	-0.80	0.42	-0.55	-0.56	0.23	-0.80	-1.15
0.2	-0.30	-1.38	-1.51	-0.24	-1.15	-1.19	-0.29	-1.48	-1.90
0.3	-0.93	-2.03	-2.21	-0.93	-1.79	-1.87	-0.78	-2.10	-2.58
0.4	-1.51	-2.67	-2.93	-1.58	-2.43	-2.62	-1.20	-2.68	-3.21
0.5	-1.97	-3.28	-3.66	-2.07	-3.06	-3.40	-1.69	-3.22	-3.73
0.6	-2.15	-3.84	-4.43	-2.24	-3.65	-4.20	-2.05	-3.73	-4.36
0.7	-1.77	-4.31	-5.17	-1.86	-4.12	-5.00	-1.71	-4.17	-5.07
0.8	-0.49	-4.62	-5.86	-0.56	-4.43	-5.75	-0.53	-4.47	-5.78
0.84	0.36	-4.68	-6.12	0.32	-4.49	-6.02	0.37	-4.53	-6.04
$T^* = 1.15$									
0.1	0.65	-0.37	-0.71	0.70	-0.29	-0.55	0.61	-0.38	-0.86
0.2	0.33	-0.71	-1.39	0.37	-0.61	-1.17	0.35	-0.73	-1.55
0.3	0.04	-1.04	-2.07	0.05	-0.92	-1.84	0.12	-1.05	-2.24
0.4	-0.17	-1.34	-2.77	-0.19	-1.23	-2.55	-0.09	-1.34	-2.85
0.5	-0.25	-1.62	-3.48	-0.27	-1.51	-3.29	-0.13	-1.59	-3.47
0.6	-0.08	-1.83	-4.25	-0.08	-1.73	-4.03	0.07	-1.78	-4.14
0.65	0.15	-1.91	-4.60	0.17	-1.81	-4.40	0.31	-1.84	-4.45
0.75	1.05	-1.98	-5.28	1.10	-1.87	-5.09	1.17	-1.89	-5.13
0.85	2.76	-1.88	-5.69	2.83	-1.76	-5.68	2.86	-1.78	-5.67
$T^* = 1.35$									
0.1	0.73	-0.28	-0.69	0.77	-0.22	-0.55	0.72	-0.29	-0.78
0.2	0.50	-0.53	-1.36	0.53	-0.46	-1.16	0.50	-0.56	-1.51
0.3	0.31	-0.77	-2.03	0.32	-0.69	-1.82	0.35	-0.80	-2.09
0.4	0.19	-0.99	-2.72	0.18	-0.91	-2.52	0.27	-1.00	-2.75
0.5	0.20	-1.17	-3.40	0.20	-1.09	-3.24	0.30	-1.16	-3.37
0.55	0.30	-1.24	-3.77	0.30	-1.16	-3.60	0.41	-1.22	-3.70
0.7	1.09	-1.34	-4.83	1.15	-1.25	-4.64	1.17	-1.29	-4.68
0.8	2.33	-1.25	-5.38	2.42	-1.15	-5.24	2.42	-1.19	-5.25
0.9	4.52	-0.98	-5.99	4.53	-0.87	-5.70	4.58	-0.91	-5.66
0.95	5.91	-0.75	-6.23	5.97	-0.64	-5.84	6.32	-0.67	-5.71

TABLE I
(Continued)

$n\sigma^3$	2nd order			1st order			MC		
	z	F/NkT	$U/N\epsilon$	z	F/NkT	$U/N\epsilon$	z	F/NkT	$U/N\epsilon$
$T^* = 2.74$									
0.1	0.98	-0.02	-0.57	0.98	-0.02	-0.52	0.97	-0.03	-0.61
0.2	0.99	-0.03	-1.16	0.99	-0.03	-1.08	0.99	-0.05	-1.21
0.3	1.05	-0.03	-1.75	1.05	-0.02	-1.67	1.04	-0.05	-1.78
0.4	1.18	0.00	-2.35	1.19	0.01	-2.28	1.20	-0.01	-2.37
0.55	1.62	0.11	-3.25	1.65	0.07	-3.16	1.65	0.06	-3.21
0.7	2.54	0.36	-3.97	2.62	0.39	-3.92	2.64	0.37	-3.90
0.8	3.59	0.63	-4.33	3.70	0.67	-4.27	3.60	0.65	-4.28
0.9	5.15	1.02	-4.53	5.24	1.07	-4.43	5.14	1.04	-4.41
1.0	7.41	1.56	-4.56	7.35	1.63	-4.31	7.39	1.58	-4.18

From the equation of state (21) we have determined also the compressibility of the system of hard spheres

$$(\partial n/\partial P) = (1 - y)^4 / (1 + 4y + 4y^2 - 4y^3 + 4y^4), \quad (24)$$

as well as an expression for the free energy of the reference system

$$(F_0 - F^*)/NkT = (4y - 3y^2)/(1 - y)^2. \quad (25)$$

In case of LJ 12-6 potential one may find analytical expression of the integrals J_1 , J_2 , K_2 and K_3

$$J_2 = 4c^{-12}/9 - 4c^{-6}/3 + 8(2)^{1/2} c^{-3}/9 - 1/3, \quad (26)$$

$$J_3 = c^{-12}/2 - 2c^{-6} + 9(2)^{2/3} c^{-4}/8 - 1/4, \quad (27)$$

$$K_2 = 16c^{-24}/21 - 32c^{-18}/15 + 16c^{-12}/9 - 0.79016c^{-3} + 1/3, \quad (28)$$

$$K_3 = 16c^{-24}/20 - 32c^{-18}/14 + 2c^{-12} - 0.81638c^{-4} + 1/4. \quad (29)$$

Substituting Eqs (22) through (29) into Eq. (16) we arrive at the expression permitting a relatively easy determination of the free energy of the system studied. For

a given temperature and density one has to evaluate c from Eq. (14). As a first estimate of c in the iteration approach we used

$$c = 2^{1/6} / [1 + (T^* \ln 2)^{1/2}]^{1/6} \quad (30)$$

following from consideration regarding the behaviour of the Mayer function for the reference potential.

Eq. (16) was then used to calculate the free energy while the explicit expressions for the integrals were evaluated numerically. Also the derivative with respect to density in Eq. (18) and the last term in Eq. (19) were evaluated numerically.

The results of the calculations for $T^* = 0.75, 1.15, 1.35,$ and 2.74 and the density ranging between 0 and 1 are shown in Table I with the pseudoexperimental data of the Monte Carlo (MC) method and the values from the Verlet-Weis first order perturbation expansion¹². From comparison it follows that the second-order terms improve the agreement of the perturbation values with the pseudoexperimental data of the compressibility factor, the free and internal energy at low temperature and densities in particular (approximately up to $\rho n^3 = 0.6$). The best improvement may be observed in case of the internal energy. Certain deterioration in region of high densities in comparison with the results of the Verlet-Weis first order expansion stems most likely from a simpler (and less accurate) expression of the radial distribution function of the system of hard spheres used in this work.

It may be concluded that the second-order term in the perturbation expansion of WCA for the Lenard-Jones 12-6 potential provides in liquid region a better prediction of the state and thermodynamic functions in comparison with previous perturbation methods.

REFERENCES

1. Mansoori G. A., Canfield F. B.: *Ind. Eng. Chem.* 62, 12 (1970).
2. Boublík T., Nezbeda I., Hlavatý K.: *Statistická termodynamika kapalin a kapalných směsí*. Academia, Prague 1974.
3. Barker J. A., Henderson D.: *J. Chem. Phys.* 47, 2856, 4714 (1967).
4. Chandler D., Weeks J. D.: *Phys. Rev. Letters* 25, 149 (1970).
5. Weeks J. D., Chandler D., Andersen H. C.: *J. Chem. Phys.* 54, 5237 (1971).
6. Smith W. R., Henderson D., Barker J. A.: *J. Chem. Phys.* 53, 508 (1970); 55, 4027 (1971).
7. Verlet L., Weis J. J.: *Phys. Rev. A* 5, 939 (1971).
8. Alder B. J., Young D. A., Mark M. A.: *J. Chem. Phys.* 56, 3013 (1972).
9. Zwanzig R. W.: *J. Chem. Phys.* 22, 1420 (1954).
10. Frisch H. L., Katz J. L., Praestgaard E., Lebowitz J. L.: *J. Phys. Chem.* 70, 2016 (1966).
11. Carnahan N. F., Starling K. E.: *J. Chem. Phys.* 51, 635 (1969).
12. Hansen J. P.: *Phys. Rev. A* 2, 221 (1970).