MICRO POTENTIAL METHOD FOR THE ESTIMATION OF THERMODYNAMIC FUNCTIONS OF DENSE FLUIDS

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A micro potential method (MPM) is proposed as a special approach to the statistical thermodynamics of dense fluids. The classical partition function of simple fluids is estimated by means of the MPM. Probability functions of micro potentials, i.e. potential energies of the particles, and corresponding generating functions are introduced to get the configurational integral of the pure fluid. In contrast to perturbation theories the MPM itself leads to a reasonable expression for the free energy of the hard-sphere system as the reference system. For the square-well fluid the MPM provides values of thermodynamic functions, which agree well with corresponding computer simulation data. The MPM results are at least of the same accuracy as those of the well known approach of Ponce and Renon [J. Chem. Phys. 64 (1976) 638].

1. Introduction

In this paper we estimate the configurational integral Q and thermodynamic functions of a classical many particle system in equilibrium. A previous paper [1] already presented a brief summary.

We consider a canonical ensemble of N identical molecules in volume V and with temperature T. Thus the partition function is given by

$$Z = (2\pi m k_B T / h^2)^{3N/2} Q / N! \, . \tag{1}$$

In this equation h is Planck's constant, k_B is Boltzmann's constant, m is the mass of the particles, and

$$Q = \int \cdots \int \exp(-U_t / k_B T) \, \mathrm{d}q_1 \cdots \mathrm{d}q_N \, . \tag{2}$$

The vector q_i symbolizes the coordinates (x_i, y_i, z_i), and U_t is the total

potential energy function of the system. With the free energy

$$F = -k_B T \ln Z \tag{3}$$

and the thermodynamic relations one gets thermodynamic quantities. We assume that the molecules of the system interact by pairwise additive forces, and the (effective) pair potential $w = w(r_{ij})$ is a function of the distance r_{ij} between the particles i and j only [2,3]. Thus, U_t can be written as

$$U_t = \sum_{i<j} w(r_{ij}) . \tag{4}$$

The starting point for the estimation of Q in our paper is a formalism of Morgan [4]. Morgan derived a probability function $P(E) \, dE$ to find the local band-edge energy E of a heavily doped semiconductor within a range dE about E. We consider the potential energy U of any given particle of the system. The probability $P(U) \, dU$ to find the "micro potential" U (potential energy U) within a range dU about U is the sum of the probabilities of all random configurations of the particles which generate a potential energy U in that range.

In the literature also electric-microfield distributions in systems of charged particles are calculated [5]. Iglesias [6] has reformulated the problem of calculating the electric-microfield distribution in a plasma so that it is equivalent to finding the pair-distribution function of a fluid interacting through a complex potential. Lado [7] solved the mean spherical model for such a fluid analytically. Powles and Fowler [8] evaluated a distribution function $P(f)$ for a Cartesian component f of the force on an atom in a Lennard-Jones liquid. Our function $P(U)$ and, particularly, generating functions of $P(U) \, dU$ and $P(U_t) \, dU_t$ are used to estimate Q (micro potential method). $P(U_t) \, dU_t$ is the probability function to have the potential energy U_t of the system within a range dU_t about U_t. If $P(U_t)$ is explicitly known, it is simple to write Q as shown in section 2.1. For instance, it seems possible to make a suitable ansatz for $P(U_t)$ to estimate Q analogously to ref. [9]. In section 2.2 we estimate the configurational integral Q approximately.

A system of hard spheres without attractive forces between the molcules is the simplest model of (dense) fluids. Such a hard-sphere system plays an important role in the perturbation theory of fluids (see for instance refs. [2,3]). In section 3.1 the free energy and the equation of state of our model are given for hard spheres. Very accurate and recent computer simulation data [10] of the hard-sphere system are known for the compressibility factor. In the fluid range for example the (analytical) Carnahan–Starling (C–S) equation of state

[11] represents the results of computer simulations well. It is possible to consider the C–S equation for hard spheres as arising from a kind of mean-field theory [12].

The square-well system is one of the simplest systems incorporating both repulsive and attractive forces. The pair potential of this system is

$$w(r) = \begin{cases} \infty, & \text{for } 0 \leq r \leq \sigma, \\ \varepsilon, & \text{for } \sigma < r < c, \quad \varepsilon < 0, \\ 0, & \text{for } r \geq c, \end{cases} \tag{5}$$

where σ is the diameter of the hard core, $|\varepsilon|$ is the well depth and c/σ is the width of the well. For pair potentials according to eq. (5) the micro potential method (MPM) allows to estimate Q (section 2.2) and thermodynamic functions (section 3.2) analytically.

The square-well system has been used as a model in testing a variety of theories and in gaining insight into the behaviour of real fluids (see ref. [13] and references therein). Square-well fluids can be taken as suitable reference systems in perturbation theories [14] for calculating thermodynamic functions and radial distribution functions.

Since the thermodynamic behaviour of a classical square-well system with the range of the well $c = 1.5\sigma$ roughly follows that of real (classical) fluids most of the studies have been carried out for this particular value of c. In the present paper (section 3.2) we also use $c/\sigma = 1.5$ to calculate thermodynamic functions, and compare the results with those of Carley and Dotson [15, 16] and those of Ponce and Renon [17]. But the most direct means for computing thermodynamic properties of classical square-well fluids are computer simulations [18–20]. We compare these and recently obtained results of Lee and Chao [21] with those of the MPM in section 3.2.

A discussion of our method and results and some conclusions follow in section 4.

2. Micro potential method

2.1. Generating functions

In order to obtain explicit expressions for the probability-density functions $P(U)$ and $P(U_t)$ we consider a system of N particles and N_0 available sites which can be occupied by the particles. It is assumed that the molecules are distributed randomly on the sites in the volume V. The average density of molecules in V is N/V and the average proability of having any molecule per

site is

$$p_0 = \frac{N/V}{N_0/V} = 1 - q_0 \, , \tag{6}$$

where N_0/V is the average density of available sites. Thus, in a given region denoted by the index i, containing g_i available sites, the probability to have exactly n_i particles is (see for example refs. [22, 23])

$$P_i(n_i) = p_0^{n_i}(1 - p_0)^{g_i - n_i} \binom{g_i}{n_i} \, , \tag{7}$$

where $\binom{g_i}{n_i}$ is the binominal coefficient expressing the number of ways in which g_i sites may be occupied by exactly n_i particles. The binominal distribution (7) corresponds to eq. (1) in ref. [4]. Here N_s is substituted by N_0/V, and small regions i are chosen. Any molecule is assumed to be in the origin of the coordinate system. If each molecule in the (small) region i contributes to the potential energy of the molecule in the origin an energy w_i, the total energy contributed by n_i molecules is $U_i = n_i w_i$, where w_i is the pair potential. Now one can introduce the generating function

$$G_i(s) = (p_0 s^{-w_i^*} + q_0)^{g_i} = \sum_{n_i} P_i(n_i) s^{-n_i w_i^*} = \sum_{U_i} P(U_i) s^{-U_i^*} \tag{8}$$

with $w_i = |\varepsilon| w_i^*$, $U_i = |\varepsilon| U_i^*$, $U = |\varepsilon| U^*$, and ε as the minimal value of the pair potential. $G_i(s)$ generates $P_i(n_i)$ from eq. (7) and s is a parameter. If we consider all regions i in V, we obtain the generating function

$$G(s) = \prod_i (p_0 s^{-w_i^*} + q_0)^{g_i} = \exp\left(\sum_i g_i \ln(p_0 s^{-w_i^*} + q_0)\right) , \tag{9}$$

and the sum extends over the entire volume V. We set $w_i = w(r)$, $g_i = 4\pi$ $(N_0/V)r^2 \, dr$ and get for the generating function $G(s)$ of $P(U) \, dU$ due to eq. (9)

$$G(s) = \exp\left(4\pi \int_0^\infty (N_0/V)r^2 \ln(p_0 s^{-w^*(r)} + 1 - p_0) \, dr\right)$$

$$= \int_{-\infty}^\infty P(U) s^{-U^*} \, dU \, , \tag{10}$$

where w^*, U^* and (later) T^* are reduced dimensionless energies, respectively temperatures with $U^*/T^* = U/k_B T$ and $w^*/T^* = w/k_B T$. Although a generating function may not yield an explicit form for the probability function, it

allows an easy access to its moments. The following expressions for the moments can be written immediately due to eq. (10):

$$\langle U^* \rangle_{av} = -(d/ds)G(s), \qquad s = 1,$$

$$\langle (U^*)^2 \rangle_{av} = (d/ds)[s(d/ds)G(s)], \qquad s = 1, \tag{11}$$

$$\langle (U^*)^m \rangle_{av} = [-s(d/ds)]^m G(s), \qquad s = 1.$$

It is possible to find an explicit expression for $P(U)$ by means of an inverse Fourier transformation. We choose $s = \exp(it^*)$ in eq. (10) (s is a complex number, t is a real number and $t^* = |\varepsilon|t$). This leads to

$$P(U) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \exp(itU) \, G(it^*) \, dt \tag{12}$$

and due to eq. (10) explicitly to

$$P(U) = \frac{1}{\pi} \int_{0}^{\infty} \exp\left(4\pi(N_0/V) \int_{0}^{\infty} r^2 \ln Y_1 \, dr\right)$$

$$\times \cos\left(Ut - 4\pi(N_0/V) \int_{0}^{\infty} r^2 \arctan Y_2 \, dr\right) dt \tag{13}$$

with

$$Y_1 = [2(N/N_0)^2 + 1 - 2(N/N_0) + 2(N/N_0)\cos(wt) - 2(N/N_0)^2 \cos(wt)]^{1/2}$$

and

$$Y_2 = (N/N_0)\sin(wt)/[1 - (N/N_0) + (N/N_0)\cos(wt)].$$

As later shown it will be sufficient to know the expression $G(s)$ in eq. (10) with $s = \exp(1/2T^*)$ to get Q and Z approximately. In order to estimate Q we introduce a generalized generating function

$$G_N^*(s_N) = \sum_{n_1} \cdots \sum_{n_M} p_1^{n_1}(1-p_1)^{g_1-n_1} \binom{g_1}{n_1} s_N^{-n_1(n_2 w_{12}^* + \cdots + n_M w_{1M}^*)}$$

$$\times p_2^{n_2}(1-p_2)^{g_2-n_2} \binom{g_2}{n_2} s_N^{-n_2(n_3 w_{23}^* + \cdots + n_M w_{2M}^*)} \cdots$$

$$\cdots p_M^{n_M}(1-p_M)^{g_M-n_M} \binom{g_M}{n_M} s_N^0$$

$$= \int_{-\infty}^{\infty} P(U_t) \, s_N^{-U_t^*} \, dU_t. \tag{14}$$

M is the number of the very small regions in V ($N/M \ll 1$), $w_{ij} = |\varepsilon| w_{ij}^*$ is the pair potential of the molecules i and j, $U_t^*/T^* = U_t/k_B T$, $n_1 + \cdots + n_M = N$, s_N is a parameter, and the N particles are again randomly distributed on the N_0 sites in V. For our purposes it is suitable to set $g_i = 1$ in all regions i ($i = 1, 2, \ldots, M$). Thus, $N_0 = M$ and all n_i become 0 or 1. For the probabilities p_i (ratios of densities) we write

$$p_i = \frac{N_i/V_i}{N_{0i}/V_{0i}} = 1 - q_i . \tag{15}$$

That is, if certain sites were occupied by any particles, then the number of particles which can occupy other sites is smaller than N. Thereby the number of sites which can be yet occupied by other particles is smaller than N_0. We consider the region i. Then N_i molecules can be distributed on N_{0i} sites in a (rest) volume $V_i \leq V$. It is $V_i = V_{0i}$, $M = N_0$, $N_i \leq N$, and $N_{0i} \leq N_0$ for $i = 1, 2, \ldots, M$. In appendix A a detailed expression is given for the p_i of eq. (15). Choosing $s_N = \exp(1/\Gamma^*)$, the exact relations

$$G_N^*(s_N) = V^{-N} Q \tag{16}$$

and

$$Q = V^N \int_{-\infty}^{\infty} P(U_t) \exp(-U_t/k_B T) \, dU_t \tag{17}$$

are derived. The term $k_B \ln[P(U_t)\, \delta U_t]$ is the difference of the entropy S of the system and the entropy S_{id} of the corresponding ideal gas.

With $s_N = \exp(it^*)$ and $t^* = |\varepsilon| t$ one gets from eq. (14)

$$G_N^*(it^*) = \int_{-\infty}^{\infty} P(U_t) \exp(-it U_t) \, dU_t , \tag{18}$$

and by means of inverse Fourier transformation

$$P(U_t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \exp(it U_t) \, G_N^*(it^*) \, dt . \tag{19}$$

$P(U_t)$ or $S - S_{id}$ can be calculated directly. This is a possible starting point to estimate Q and thermodynamic functions according to eq. (17). We prefer another way. In appendix B, Q is derived from G_N^* of eq. (14) with p_i of eq.

(15). The exact result is

$$Q = V^N \int\limits_{-\infty}^{\infty} \cdots \int\limits_{-\infty}^{\infty} \left(\prod_{j=1}^{N} [P_j(U_j|U_{j-1}| \cdots |U_1) \, s^{-U_j^*}] \right) dU_1 \ldots dU_N , \qquad (20)$$

where

$$s = s_N^{1/2} = \exp(1/2T^*) , \qquad U_j^*/T^* = U_j/k_B T , \qquad \sum_{j=1}^{N} U_j = 2U_t ,$$

and

$$P_j(U_j|U_{j-1}| \cdots |U_1) \, dU_j$$

is the conditional probability to have a potential energy U_j for the particle of number j, if the particle of number 1 has the potential energy U_1, the second particle has the potential energy U_2, etc., and the particle of number $j - 1$ has the potential energy U_{j-1}. By means of eq. (10) and eq. (20) we shall give approximate formulae for Q.

2.2. Approximate estimations of the configurational integral

We estimate Q from eq. (20) using the approximation

$$Q = V^N \left(\int\limits_{-\infty}^{\infty} P(U) \, s^{-U^*} \, dU \right)^N = V^N [G^+(s)]^N , \qquad (21)$$

where

$$G^+(s) = \exp\left(\sum_i g_i \ln(p_i s^{-w_i^*} + q_i) \right) \qquad (22)$$

is a modified generating function. Assuming again that $g_i = 1$ for all regions i and setting $w_1^* = 0$, p_i can be taken from eq. (15). Because N, $N_0 \gg 1$ and $w(r) \, r^3 \to 0$ for $r \to \infty$, the quantities p_i, q_i in eq. (22) can be replaced by p_0 and q_0, respectively, for all i. Thus, $G^+(s)$ of eq. (22) becomes $G(s)$ of eq. (9) and according to eq. (10) it follows from eq. (21) that

$$Q = V^N \left[\exp\left(4\pi(N_0/V) \int\limits_0^{\infty} r^2 \ln(p_0 \, e^{-w(r)/2k_B T} + 1 - p_0) \, dr \right) \right]^N . \qquad (23)$$

In order to take into account the facts that the particles have a finite volume and that the $P_j(U_j) \, dU_j$ in eq. (20) are conditional probabilities we assume

$N_0 = Vf$ in eq. (23) with $\sigma^3 f \approx 1$, $w(\sigma) = 0$, and σ is the diameter of the molecules. In the following part of this paper hard-core fluids, particularly square-well fluids are considered. For example $f = 2^{1/2}/\sigma^3$ corresponds to a regular close packing of N_0 hard spheres in V. In this case using eqs. (1), (3), (23), the square-well potential (5) and thermodynamic relations, one gets

$$
G = V^N \exp\Big(4\pi Nf(\sigma^3/3)\{\ln(1 - N/Vf)
$$
$$
+ [(c/\sigma)^3 - 1]\ln[(N/Vf)\,e^{|\varepsilon|/2k_BT} + 1 - N/Vf]\}\Big)
\tag{24}
$$

and qualitatively correct results for the thermodynamic functions. In order to improve our model, the expression $4\pi r^2(N_0/V)$ in eq. (23) is substituted by $4\pi r^2 A(r)(N_0/V)$, $N_0 = Vf$ and it is $f = (2^{1/2}/\sigma^3)f^*$, where f^* is a reduced quantity. Due to eq. (23) one can write then

$$
Q = V^N \exp\Big(4\pi Nf \int_0^\infty A(r)\,r^2 \ln[(N/Vf)(e^{-w(r)/2k_BT} - 1) + 1]\,dr\Big)
\tag{25}
$$

with an appropriate function $A(r)$. We remark that $P(U_t)$ can be estimated by means of eq. (19) for the function

$$
G_N^*(s_N) = [G(s)]^N
$$
$$
= \exp\Big(4\pi N(N_0/V) \int_0^\infty A(r)\,r^2 \ln[(N/N_0)s^{-w^*(r)} + 1 - (N/N_0)]\,dr\Big),
\tag{26}
$$

where $s_N = \exp(it^*) = s^2$, $t^* = |\varepsilon|t$ and $G(s)$ is the generating function in eq. (10), modified by a function $A(r)$. We get

$$
P(U_t) = \frac{1}{\pi} \int_0^\infty \exp\Big(4\pi N(N_0/V) \int_0^\infty A(r)\,r^2 \ln Y_1^*\,dr\Big)
$$
$$
\times \cos\Big(U_t - 4\pi N(N_0/V) \int_0^\infty A(r)\,r^2 \arctan Y_2^*\,dr\Big)\,dt
\tag{27}
$$

with

$$
Y_1^* = [2(N/N_0)^2 + 1 - 2(N/N_0) + 2(N/N_0)\cos(wt/2)
$$
$$
-2(N/N_0)^2 \cos(wt/2)]^{1/2}
$$

and

$$
Y_2^* = (N/N_0)\sin(wt/2)/[1 - (N/N_0) + (N/N_0)\cos(wt/2)].
$$

Now we set $f^* = (2^{1/2}\alpha)^{-1}$ with $\alpha = \pi^2/12$ from a random close packing [24–26] of N_0 hard spheres in $V = N_0\sigma^3\alpha$. Recently Berryman [27] showed that for a random close packing the packing fraction is given by $\eta = 0.64 \pm 0.02$. This value of η corresponds to $\alpha = 0.8181$. For $r \leq \sigma$ it is plausible that A has a value $A_0 < 1$ because one particle is in the origin $r = 0$ and this site is occupied. Thus, the number of available sites in a sphere of diameter 2σ is

$$A_0[(\alpha\sigma^3)^{-1}(4\pi\sigma^3/3)] = [(\alpha\sigma^3)^{-1}(4\pi/3)][\sigma^3 - (\sigma_\alpha/2)^3] - 1 , \tag{28}$$

where $(\alpha\sigma^3)^{-1}$ is the average density of sites in the volume V and $\sigma_\alpha \approx \sigma$. Then it becomes

$$A_0 = 1 - (\sigma_\alpha/2\sigma)^3 - 3\alpha/4\pi . \tag{29}$$

In order to explain σ_α we consider a large volume V. It contains N_0 sites ($N_0 \gg 1$) which can be occupied by molecules. These sites are uniformly distributed, that is, they are distributed as molecules which have no volume and do not interact. The distance distribution function of the nearest site is

$$\omega(r) = 4\pi r^2 n \exp(-4\pi r^3 n/3) \tag{30}$$

with $n = N_0/V$ and r as the distance between the origin and the nearest site [28]. For the maximum value of $\omega(r)$ one can write

$$r_{\max} = [2 \times 2^{1/2}\pi(V_0/V)]^{-1/3}\sigma , \tag{31}$$

where $V_0 = N_0\sigma^3/2^{1/2}$. Firstly we set $(V_0/V) = (2^{1/2}\alpha)^{-1}$ in eq. (31). This corresponds to a random close packing of N_0 hard spheres in V. Thus, one has $r_{\max} = 0.5078\sigma$. Secondly we use $\sigma_\alpha/2 = 0.5078\sigma$ in eq. (29) and get $A_0 = 0.6727$. The function $A(r)$ is now known for $r \leq \sigma$ ($A = A_0$). For $\sigma < r < x_c$ with the parameter $x_c \leq 1.5\sigma$, the densest possible packing of sites (N_0 spheres) is assumed, i.e. $A = 2^{1/2}\alpha$. For $r \geq x_c$ the above introduced average density of sites is assumed (random close packing; $A = 1$). This leads to the equation

$$A_0 = 1 - [(x_c/\sigma)^3 - 1](\alpha 2^{1/2} - 1) \tag{32}$$

because the average density of available sites in $0 \leq r \geq x_c$ is $(1/\alpha\sigma^3)$. With $A_0 = 0.6727$ and using eq. (32) the parameter x_c is equal to 1.443σ.

Choosing the function $A(r)$ in the just presented manner and using eq. (32) then eq. (25) for Q yields eq. (7) in ref. [1]. But we are especially interested in

a square-well system according to eq. (5). Our model leads to

$$Q = V^N \exp\Big((4\pi 2^{1/2}/3)Nf^*\{A_0 \ln(1 - V_0/Vf^*)$$

$$+ B_0[(c/\sigma)^3 - A_0] \ln[(V_0/Vf^*)(e^{|\varepsilon|/2k_BT} - 1) + 1]\}\Big) \tag{33}$$

with $V_0 = N\sigma^3/2^{+1/2}$, $c/\sigma = 1.5$ and three parameters A_0, B_0, f^*. In the case discussed above the parameter B_0 was $B_0 = 1$ and it is $f^* = 0.8597$, $A_0 = 0.6727$. This is the first version of the micro potential method (MPM) denoted by MPM1. Another possibility to explain A_0 and f^* in eq. (33) is the following one: A_0 is set equal to 0.5 to get the exact second virial coefficient of a hard-sphere system, $f^* = 0.795$ is chosen to fit the equation of state of Carnahan and Starling [11] for $V_0/V \leqslant 0.667$, and it is $B_0 = 1$.

This is a second version of the MPM (MPM2). A third version (MPM3) with $B_0 > 1$ is described in section 3.2.

3. Thermodynamic functions

3.1. Hard spheres

Choosing $\varepsilon = 0$ in eq. (33) we get Q of the MPM for the hard-sphere system. According to eqs. (1), (3) and (33) one finds

$$(F - F_{id})/Nk_BT = -(4\pi 2^{1/2}/3)f^*A_0 \ln[1 - (V_0/V)/f^*] \tag{34}$$

for the free energy, where F_{id} is the free energy of the ideal gas. Using eq. (34) and the relation

$$p = -(\partial F/\partial V)_T \tag{35}$$

the compressibility factor of a hard-sphere system is

$$pV/Nk_BT = 1 + (4\pi 2^{1/2}/3)A_0(V_0/V)[1 - (V_0/V)/f^*]^{-1} . \tag{36}$$

In the fluid range a simple and nevertheless good approximation is the Carnahan–Starling (C–S) equation of state [11]. The C–S equation can be further improved by adapting to the lower virial coefficients, whose exact values we find for instance in ref. [29]. In a paper of Boublik and Nezbeda [30]

a modified C–S equation of state of Kolafa for the fluid range is given by

$$pV/Nk_BT = (1 + \eta + \eta^2 - \tfrac{2}{3}\eta^3 - \tfrac{2}{3}\eta^4)/(1 - \eta)^3 \tag{37}$$

with $\eta = N\sigma^3\pi/6V$. This equation is significantly better than the C–S equation. From eq. (37) one gets

$$(F - F_{id})/Nk_BT = \tfrac{5}{3}\ln(1 - \eta) + [\eta/6(1 - \eta)^2](34 - 33\eta + 4\eta^2). \tag{38}$$

For the MPM1, $(F - F_{id})/Nk_BT$ from eq. (34) is plotted in fig. 1. This function is compared with that of the Percus–Vevick theory given by Ponce and Renon [17] and that which follows from the MPM2. Reliable values for the free energy from eq. (38) are given, too.

For a system of hard rods the corresponding one-dimensional form of eq. (9) is the starting point to derive
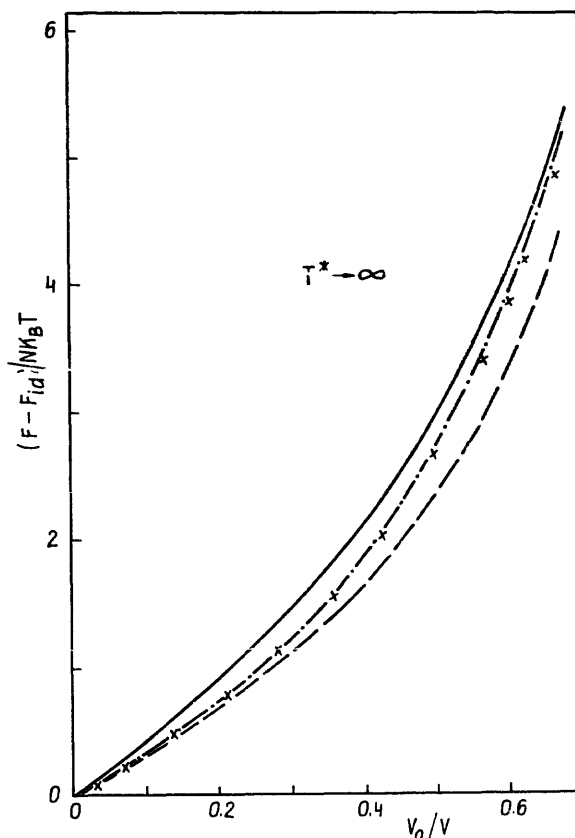
$$Q = V^N \exp[N \ln(1 - N\sigma/V)] \tag{39}$$

Fig. 1. Reduced excess free energy versus reduced density for the hard-sphere system. —— MPM1 results; – – MPM2 results; –·– PY results given by ref. [17]; ××× Kolafa's results from eq. (38).

and

$$pV/Nk_{B}T = 1 + N\sigma/(V - N\sigma) , \tag{40}$$

where σ is the length of the N hard rods confined to a line of length V. Our eq. (40) is Tonks' exact equation of state for the many-body system [31].

With $B_0 = 1$, $f^* = 1/2^{1/2}\alpha$ and $\alpha = \pi^2/12$, eq. (33) results in eq. (9) of ref. [1]. There $A_0 = 0.670$ was chosen to fit the C–S equation for $V_0/V \leqslant 0.667$.

By means of a cell theory Gurikov [32] found an expression similar to our eq. (36) with a slightly changed parameter $A_0 = 0.6738$ and $f^* = 0.8597$.

A modified cell theory of Vörtler [33] is applied to hard spheres. The result is

$$pV/Nk_{B}T = 1 + 0.5[s/(s - 1)][\alpha 2^{1/2}(V_0/V)]^{1/3}/[1 - (\alpha 2^{1/2}V_0/V)^{1/3}] \tag{41}$$

with $\alpha = 0.8225$ and $s = 2.134$. In the case $s = 2$ and $\alpha = 2^{-1/2}$ one obtains the equation of state from the corresponding conventional lattice–cell theory using the one-particle partition function approximation [34].

Table I shows the values of the Kolafa hard-sphere equation (37), which represents simulation data in a very accurate manner. The second column comprises the values of the compressibility factor via eq. (36) for the MPM1. In the third column we find the values of the modified cell theory (MCT) of Vörtler [33] according to eq. (41). The MPM values in the second column are not far from those of the first column. For comparison extrapolated values of Carley [15] for $T^* \to \infty$ and the results of Gurikov [32] are given, too.

Fig. 2 shows graphs of $pV/Nk_{B}T$ for different approaches (explanation as in fig. 1). The MPM1 (full line) matches the generally accepted simulation results.

Table I
Compressibility factor of the hard-sphere system in dependence on the reduced density.

| V_0/V	Kolafa eq. (37)	MPM1 eq. (36)	Vörtler eq. (41)	Carley [15]	Gurikov [32]
0.07071	1.2397	1.3070	1.7241	1.241	1.3075
0.11111	1.4085	1.5085	1.9622	1.409	1.5093
0.17500	1.7359	1.8756	2.344	1.735	1.8770
0.2500	2.244	2.405	2.847	2.24	2.407
0.3000	2.683	2.836	3.238	2.67	2.839
0.3536	3.270	3.393	3.730	3.25	3.397
0.4243	4.295	4.338	4.545	4.24	4.343
0.4950	5.727	5.649	5.657	5.62	5.657
0.5657	7.770	7.592	7.285	7.57	7.602
0.62500	10.194	10.123	9.391	9.87	10.138
0.6670	12.48	12.86	11.66	12.1	12.88
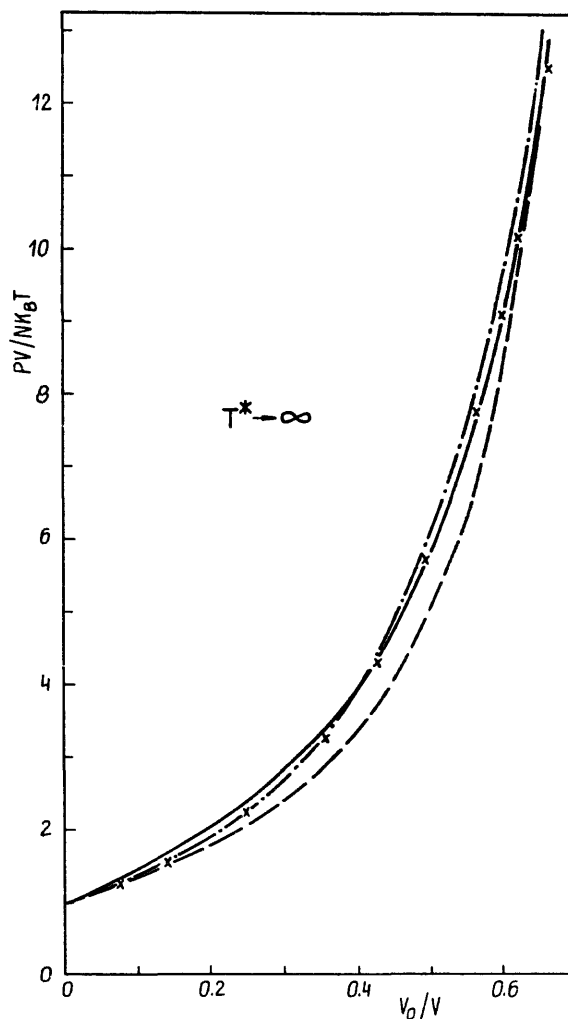
Fig. 2. Compressibility factor versus reduced density for the hard-sphere system. —— MPM1 results; — — MPM2 results; — · — PY results given by ref. [17]; × × × Kolafa's results from eq. (37).

3.2. Square-well system

The approximation of Q from eq. (24) leads to an expression for the excess free energy $F - F_{id}$. This is

$$(F - F_{id})/Nk_B T = -(4\pi 2^{1/2}/3) \ln(1 - V_0/V)$$

$$-(4\pi 2^{1/2}/3)[(c/\sigma)^3 - 1]$$

$$\times \ln\{1 + (V_0/V)[\exp(|\varepsilon|/2k_B T) - 1]\} . \tag{42}$$

Sandler and Lee [35] suggested a model of the total coordination number N_c

for square-well fluids based on the lattice gas theory. By means of N_c they get

$$(F - F_{id})/Nk_BT = (F_{hs} - F_{id})/Nk_BT$$
$$- z_M \ln\{1 + (V_0/V)[\exp(|\varepsilon|/2k_BT) - 1]\} , \qquad (43)$$

where F_{hs} is the free energy of the hard-sphere system and z_M is the maximum coordination number. For the $c/\sigma = 1.5$ square-well fluid, the lattice coordination number is $z_M = 18$. The attraction terms of eq. (42) and eq. (43) are equal except for a multiplicative constant.

Our improved model results in eq. (33). Via eqs. (1), (2), (3), (33) and the relations

$$p = k_BT\left(\frac{\partial}{\partial V} \ln Z\right)_T \qquad (44)$$

for the pressure, and

$$U_{int} = k_BT^2\left(\frac{\partial}{\partial T} \ln Z\right)_V \qquad (45)$$

for the internal energy, we get the reduced excess free energy

$$(F - F_{id})/Nk_BT = -(4\pi2^{1/2}/3)f^*\{A_0 \ln(1 - D_V)$$
$$+ B_0[(c/\sigma)^3 - A_0] \ln D_1\} , \qquad (46)$$

the compressibility factor

$$pV/Nk_BT = 1 + (4\pi2^{1/2}/3)f^*\{A_0D_V/(1 - D_V)$$
$$- B_0[(c/\sigma)^3 - A_0](D_1 - 1)/D_1\} , \qquad (47)$$

and the reduced excess internal energy

$$(U_{int} - U_{id})/N|\varepsilon| = -(4\pi2^{1/2}/6)f^*B_0[(c/\sigma)^3 - A_0]D_VD_T/D_1 , \qquad (48)$$

where

$$D_V = (V_0/V)/f^* , \quad \ln D_T = 1/2T^* ,$$
$$D_1 = D_V(D_T - 1) + 1 , \quad T^* = k_BT/|\varepsilon| ,$$

and U_{id} is the internal energy of the ideal gas.

For the parameters A_0, f^* in eqs. (46), (47), (48) we have taken the same MPM values as in the case of the hard-sphere system. For the MPM2 eq. (33) leads to a partition function and to thermodynamic functions, which are already given in ref. [36]. MPM1 and MPM2 are characterized by $B_0 = 1$. An improved version of the MPM1 should use $B_0 > 1$.

For $T^* \to \infty$ the reduced excess internal energy of eq. (48) becomes

$$\lim_{T^* \to \infty} [(U_{int} - U_{id})/N|\varepsilon|] = -(4\pi 2^{1/2}/6)B_0[(c/\sigma)^3 - A_0](V_0/V). \qquad (49)$$

Generally spoken, for a square-well system

$$\lim_{T^* \to \infty} [(U_{int} - U_{id})/N|\varepsilon|] = -\langle M \rangle /N$$

is the second coefficient A_1 in a Taylor expansion of the reduced excess Helmholtz free energy with respect to the infinite temperature limit and depends only on the density [18]. The first term of the series is A_0^E/Nk_BT, where A_0^E means the excess hard sphere free energy. The term $\langle M \rangle$ is a statistical average of the number M of pairs of interacting particles, which have the coordination number $2\langle M \rangle /N$.

At close and regular packing each particle has 12 nearest neighbours and 6 second-nearest neighbours in its well. Hence it seems to be possible and reasonable to set $(U_{int} - U_{id})/N|\varepsilon| = -9$ in eq. (49) to get B_0. Because $(V_0/V) \to 1$ in this limit it is $B_0 = 1.124$. Thus, an improved version of the MPM (the MPM3) results in $A_0 = 0.6727$, $f^* = 0.8597$, and $B_0 = 1.124$. For the model of eq. (43) the quantity $(U_{int} - U_{id})/N|\varepsilon|$ has the limit value -9, too. Similar, but more complicated expressions for the thermodynamic functions are given by Lee and Chao [21]. They obtain

$$F/Nk_BT = F_{hs}/Nk_BT - (z_0/2\gamma 2^{1/2})(V/V_0)\ln[1 + 2^{1/2}(V_0/V)(\Omega - 1)] \qquad (50)$$

in their eq. (5), in which

$$\Omega = \exp(\gamma|\varepsilon|/k_BT),$$

$$z_0 = (4\pi/3)[(c/\sigma)^3 - 1](1 + 0.57 \times 2^{1/2}V_0/V)2^{1/2}V_0/V,$$

$$\gamma = 1 + 0.1044 \times 2^{1/2}(V_0/V) - 5.6938(V_0/V)^2 + 4.7570 \times 2^{1/2}(V_0/V)^3.$$

but F_{hs} is taken from the approach of Carnahan and Starling [11], and instead of γ Lee and Chao use the symbol α.

In fig. 3 the reduced free energy, calculated via eq. (46), is plotted against the reduced density for the three versions of the MPM and is compared with
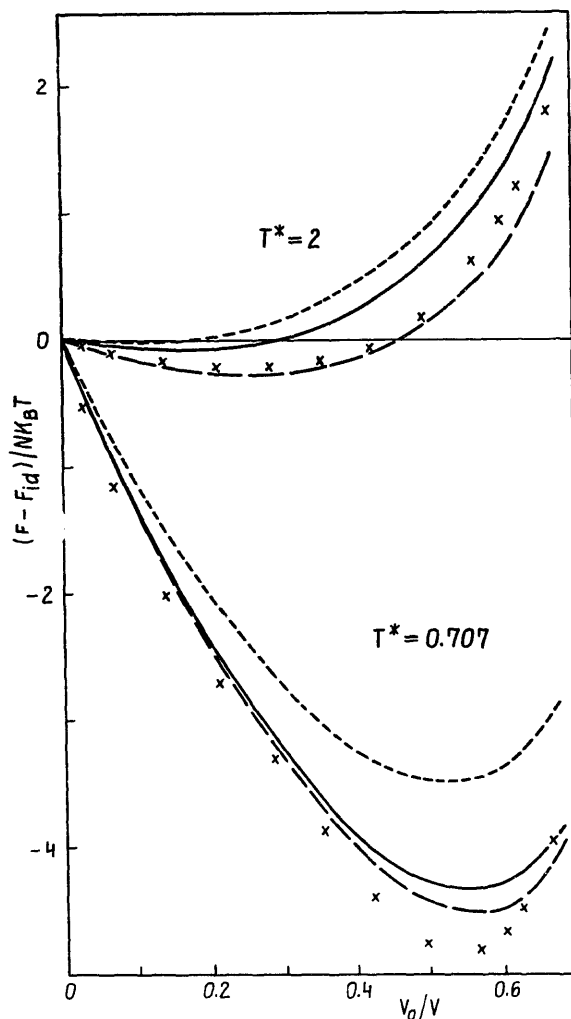
Fig. 3. Reduced excess free energy versus reduced density for the square-well system with $c/\sigma = 1.5$. —— MPM3 results; ---- MPM1 results; -- MPM2 results; $\times\times\times$ four-term series approximation results from ref. [18].

results of Alder et al. [18]. In fig. 4 the reduced free energy, calculated by the MPM3, are compared with results of Lee and Chao, eq. (50), and Ponce and Renon [17]. Ponce and Renon found an analytical equation for the Helmholtz free energy of a pure fluid. They use the successful perturbation theory of Barker and Henderson (see for instance ref. [2]) and a square-well potential with $c/\sigma = 1.5$. For the same pair potential Carley and Dotson [15, 16] computed thermodynamic properties in liquid and vapour regions. Their results appear to be reasonably accurate.

Figs. 5 and 6 show calculated values for the compressibility factor of square-well fluids of the 3 versions of the micro potential method and other theoretical approaches [15–17]. The exact simulation data [18–20] are given for
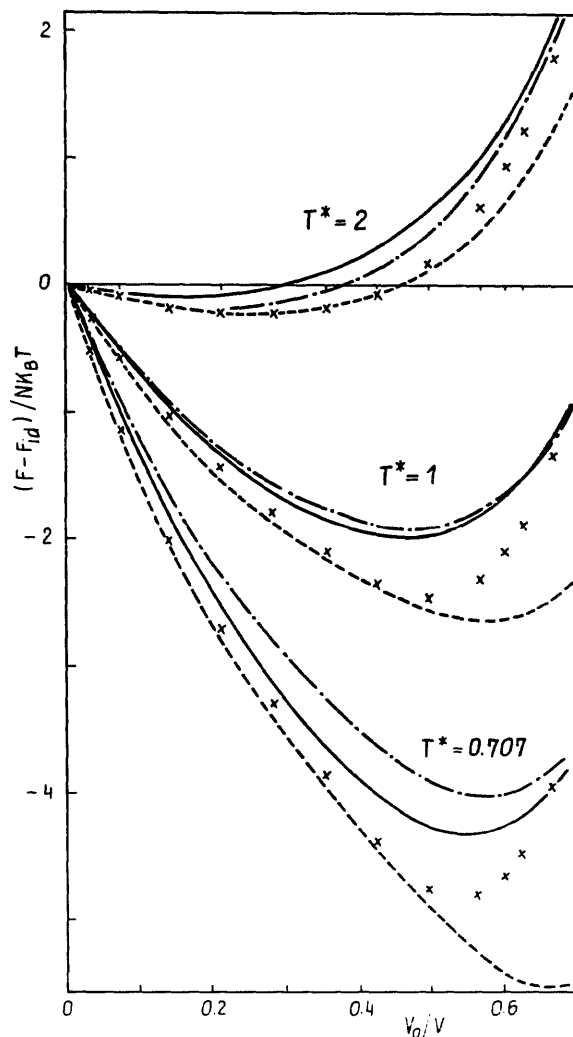
Fig. 4. Reduced excess free energy versus reduced density for the square-well system with $c/\sigma = 1.5$. —— MPM3 results; —·— results from ref. [17]; - - - - results from eq. (50); ×××
four-term series approximation results from ref. [18].

comparison. Fig. 7 shows the dependence of the excess internal energy $(U_{int} - U_{id})/N|\varepsilon|$ on the reduced temperature T^* for different V_0/V via eq. (48) and the parameter sets used above. As we see in fig. 8 the results of the MPM3 reproduce the simulation data of refs. [18, 19, 37] more accurately than the results of some other theories. They are comparable in accuracy with those of Carley and Dotson [15, 16] for $V_0/V > 0.354$.

4. Discussion and conclusions

The thermodynamic functions of a fluid many particle system are estimated in terms of the micro potential distribution function $P(U)\,dU$, that is, of the
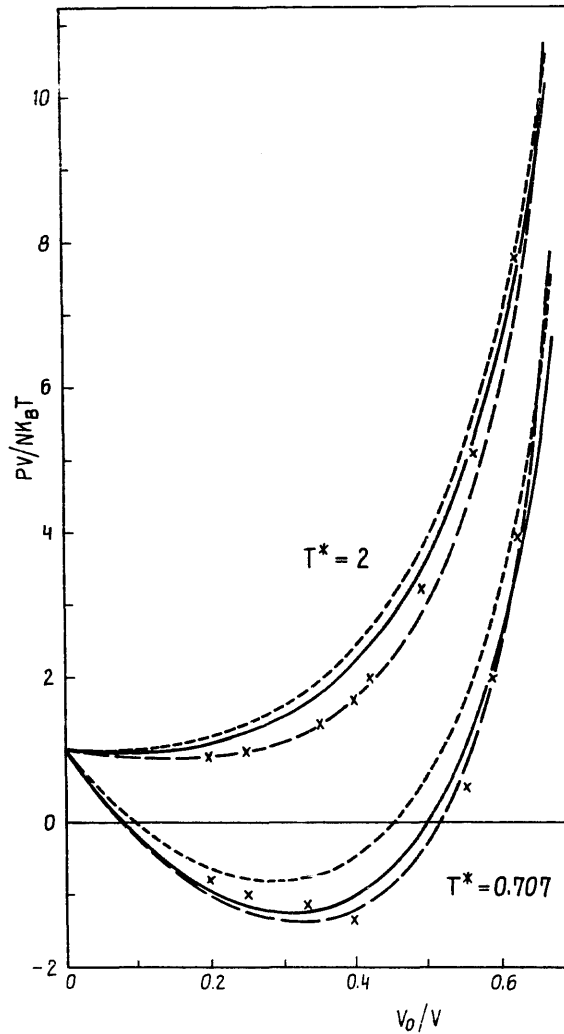
Fig. 5. Compressibility factor versus reduced density for the square-well system with $c/\sigma = 1.5$.
—— MPM3 results; ---- MPM1 results; --MPM2 results; $\times\times\times$ computer simulation data [18–20].

probability function to find system particles with a potential energy between U and $U + dU$. Thereby, it is assumed that the total potential U_t of the system is the sum of pairwise additive interaction potentials (see eq. (4)). By introduction of generating functions G and G_N^* one can evaluate $P(U)$ and $P(U_t)$ exactly. The generating functions are related directly to the configurational integral Q. Thus, it is not necessary to calculate the probability density functions $P(U_t)$ or $P(U)$ explicitly. $P(U_t)$ is proportional to $\exp[(S - S_{id})/k_B]$ with $(S - S_{id})$ as the excess entropy of the canonical ensemble. It is interesting to ask whether $P(U_t)$ and Q can be estimated in a similar way under more general conditions than given by eq. (4). G_N^* also enables us to find an exact
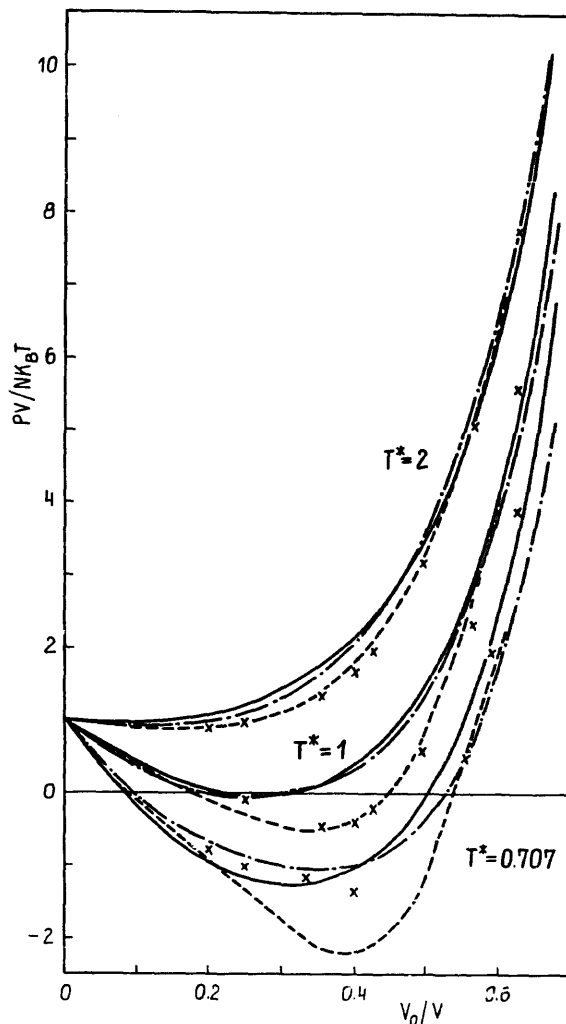
Fig. 6. Compressibility factor versus reduced density for the square-well system with $c/\sigma = 1.5$. —— MPM3 results; —·— results from ref. [17]; ---- results from refs. [15, 16]; ××× computer simulation data [18–20].

relation between the configurational integral Q and conditional probabilities $P_j(U_j)\,\mathrm{d}U_j$ (eq. (20) in section 2.1).

The assumption that these probabilities are not conditional probabilities permits an easy estimation of Q by means of G. Then we take into account the fact that the particles have a finite volume and the $P_j(U_j)\,\mathrm{d}U_j$ are conditional probabilities by restricting the number of sites in V. Introducing a suitable and simply chosen function $A(r)$ the function G is modified and we get an approximation for Q (section 2.2).

In this paper the MPM is applied to a square-well fluid providing analytical expressions for Q (eq. (33)) and thermodynamic functions (section 3). For
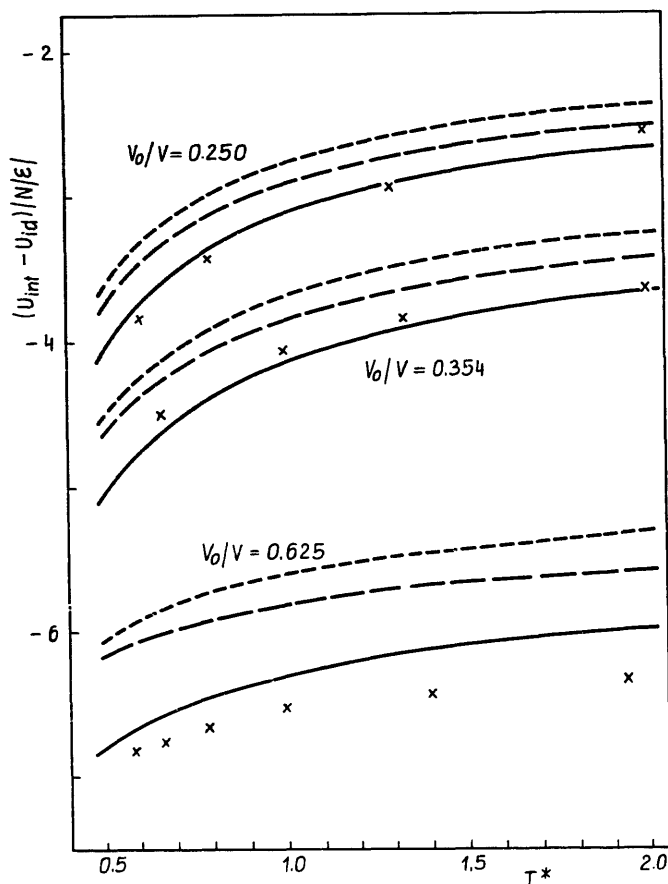
Fig. 7. Reduced excess internal energy versus reduced temperature for the square-well system with $c/\sigma = 1.5$. —— MPM3 results; ---- MPM1 results; -- MPM2 results; ××× × computer simulation data [18, 19, 37].

$T^* \to \infty$ the hard-sphere results are recovered. Eq. (33) contains three parameters A_0, f^* and B_0. We do not try to adjust the parameters in a formal way or to introduce a larger number of parameters. Comparing the thermodynamic functions for different parameters or several models we consider the properties, especially, at higher densities. Exact computer simulation results are cited for comparison.

Three versions of the MPM are considered. The original version MPM1 leads to good results for the reduced excess free energy and the compressibility factor for a hard-sphere fluid ($T^* \to \infty$) as shown in figs. 1 and 2. For $T^* \leqslant 2$ the MPM2 ($B_0 = 1$) provides better values for these quantities (see figs. 3–5) than the MPM1. But all parameters of the MPM1 ($B_0 = 1$) are derived by physical arguments. Choosing $B_0 > 1$ one can improve our results (MPM3). By means of eq. (49) we suggest for $T^* \to \infty$ and $c/\sigma = 1.5$ the value $B_0 = 1.124$. A comparison with Alder and Hecht [38] confirms this value. The effect of
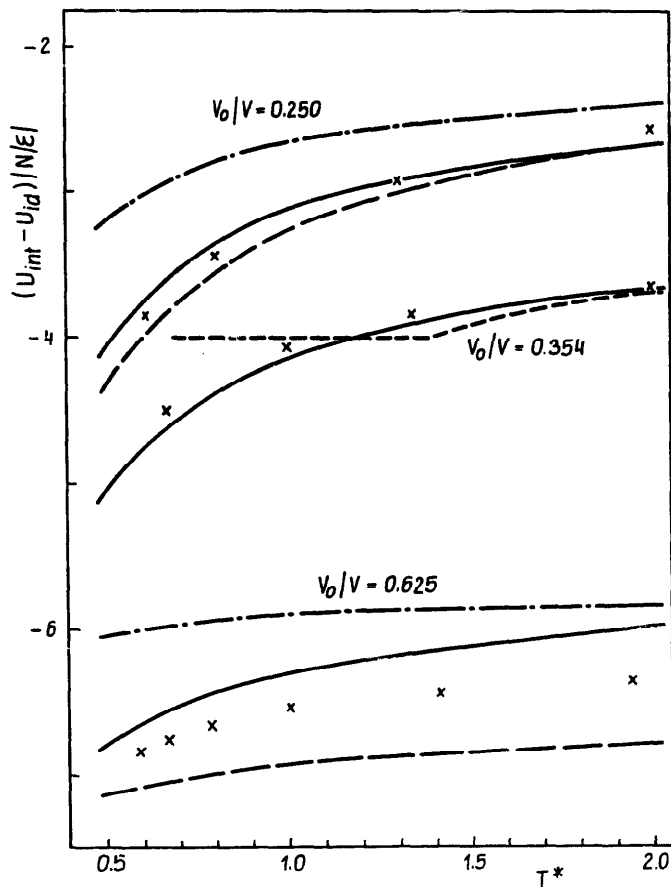
Fig. 8. Reduced excess internal energy versus reduced temperature for the square-well system with $c/\sigma = 1.5$. —— MPM3 results; ---- results from refs. [15, 16]; -- results from ref. [21]; -·- results from ref. [17]; ××× computer simulation data [18, 19, 37].

attractive forces is now taken into account to adjust the parameter B_0. The version MPM3 is a clear improvement of the MPM1 (see figs. 3, 5 and 7). The parameters A_0 and f^* are explained in the same way as in the MPM1. Of course, a corresponding determination of B_0 in eq. (49) at the density of a random close packing would be desirable. Nevertheless, the version MPM3 is likely the best version of the MPM for square-well fluids. However, in this paper we do not intend to find the optimized value of B_0. In our opinion it is more important to improve the MPM model itself.

Comparisons with the values of thermodynamic functions estimated by Carley and Dotson [15, 16], Ponce and Renon [17], Lee and Chao [21], and with corresponding computer simulation data [10, 18–20, 37] show that the micro potential method leads to results of about equal accuracy for square-well fluids (see also table I, figs. 4, 6 and 8). Our model is fairly simple and yields reasonable results. The description of more general hard-core fluids by means

of the MPM is straightforward. Summarizing we state that generating functions are a successful approach to estimate partition functions and thermodynamic quantities.

Acknowledgement

Appendix A

The detailed expression of eq. (15) is

$$p_i = \frac{N_i/V_i}{N_{0i}/V_{0i}} = \frac{N - \sum_{j=0}^{i-1} n_j}{N_0 - i + 1} = 1 - q_i ,$$ (A.1)

where $V_i = V_{0i}$, $g_i = 1$ for all small regions i ($i = 1, 2, \ldots, M$), n_j is equal to 0 or 1, $n_1 + n_2 + \cdots + n_M = N$, and $M = N_0$. Of course, $p_i = 0$ for all i, if

$$\sum_{j=0}^{i-1} n_j \geq N , \quad \text{and} \quad q_i = 0 \quad \text{for all } i , \quad \text{if } N_0 - i + \sum_{j=0}^{i-1} n_j < N .$$

Thereby, $n_0 = 0$ and $g_0 = 0$. Choosing $g_i = 1$ in all regions i ($N_0 = M$) one gets from eq. (14)

$$G_N^*(s_N) = \sum_{n_1} \sum_{n_2} \cdots \sum_{n_M} p_1^{n_1}(1 - p_1)^{1 - n_1} s_N^{-n_1(n_2 w_{12}^* + \cdots + n_M w_{1M}^*)}$$

$$\times p_2^{n_2}(1 - p_2)^{1 - n_2} s_N^{-n_2(n_3 w_{23}^* + \cdots + n_M w_{2M}^*)} \cdots p_M^{n_M}(1 - p_M)^{1 - n_M} s_N^0$$

$$= \int_{-\infty}^{\infty} P(U_t) s_N^{-U_t} \, dU_t .$$ (A.2)

We estimate the generalized generating function G_N^* in eq. (A.2) by means of

the probabilities defined by eq. (A.1). This gives

$$G_N^*(s_N) = \sum_{i_1} \sum_{i_2} \cdots \sum_{i_N} (s_N^{-w_{i_1 i_2}^* - w_{i_1 i_3}^* - \cdots - w_{i_{N-1} i_N}^*} p_{i_1} \cdots p_{i_N} A_q),$$

$$i_1 < i_2 < \cdots < i_N,$$ (A.3)

with

$$A_q = \prod_{i_1=1}^{i_1-1} \prod_{k_2=i_1+1}^{i_2-1} \cdots \prod_{k_N=i_{N-1}+1}^{i_N-1} (q_{k_1} \cdots q_{k_N}),$$ (A.4)

where $k_j < k_{j+1} - 1$ for $j = 1, 2, \ldots, N$. The following equations hold:

$$p_{i_1} p_{i_2} \cdots p_{i_N} = [N/(N_0 - i_1 + 1)][(N-1)/(N_0 - i_2 + 1)] \cdots$$
$$\cdots [1/(N_0 - i_N + 1)]$$ (A.5)

and

$$\prod_{k_1=1}^{i_1-1} q_{k_1} = [(N_0 - N)/N_0][(N_0 - N - 1)/(N_0 - 1)] \cdots$$
$$\cdots [(N_0 - N - i_1 + 2)/(N_0 - i_1 + 2)],$$

$$\prod_{k_2=i_1+1}^{i_2-1} q_{k_2} = [(N_0 - N - i_1 + 1)/(N_0 - i_1)][(N_0 - N - i_1)/(N_0 - i_1 - 1)] \cdots$$
$$\cdots [(N_0 - N - i_2 + 3)/(N_0 - i_2 + 2)],$$ (A.6)

$$\prod_{k_3=i_2+1}^{i_3-1} q_{k_3} = [(N_0 - N - i_2 + 2)/(N_0 - i_2)][(N_0 - N - i_2 + 1)$$
$$/(N_0 - i_2 - 1)] \cdots [(N_0 - N - i_3 + 4)/(N_0 - i_3 + 2)],$$

$$\cdots$$

$$\prod_{k_N=i_{N-1}+1}^{i_N-1} q_{k_N} = [(N_0 - i_{N-1} - 1)/(N_0 - i_N - 1)][(N_0 - i_{N-1} - 2)$$
$$/(N_0 - i_{N-1} - 1)] \cdots [(N_0 - i_N + 1)/(N_0 - i_N + 2)].$$

Thus we can write

$$p_{i_1} \cdots p_{i_N} A_q = \frac{N!(N_0 - N)(N_0 - N - 1) \cdots (N_0 - i_N + 1)}{N_0(N_0 - 1) \cdots (N_0 - i_N + 2)(N_0 - i_N - 1)}$$ (A.7)

and according to eq. (A.3)

$$G_N^*(s_N) = \sum_{i_1} \cdots \sum_{i_N} (s_N^{-w_{i_1 i_2}^* - w_{i_1 i_3}^* - \cdots - w_{i_{N-1}^* i_N}^*})$$

$$/[(N_0 - N + 1)(N_0 - N + 2) \cdots N_0]$$

$$= \sum_{i_1} \cdots \sum_{i_N} s_N^{-w_{i_1 i_2}^* - w_{i_1 i_3}^* - \cdots - w_{i_{N-1}^* i_N}^*} (N_0 - N)! / N_0! \,, \tag{A.8}$$

where $i_1, i_2, \ldots, i_N$ are now any different numbers from 1 to $M = N_0$. But because the limit of the quotient of any given function $f(N, T^*)$ and N_0 is zero as N_0 tends to infinity $(N/N_0 \ll 1)$, $n! = (n/e)^n (2\pi n)^{1/2}$ for large n, $(1 - x)^{1/x} = e^{-1}$ for $x \to 0$, $s_N = \exp(1/T^*)$, $w_{ii} = \infty$ for all i and $\Delta V = V/N_0$, one gets the exact equations

$$G_N^*(s_N) = V^{-N} \int \cdots \int \exp(-U_t/k_B T) \, dq_1 \ldots dq_N = V^{-N} Q \tag{A.9}$$

and

$$Q = V^N \int_{-\infty}^{\infty} P(U_t) \exp(-U_t/k_B T) \, dU_t \,. \tag{A.10}$$

Eqs. (A.9) and (A.10) are the relations (16) and (17) of section 2.1 in this paper.

Appendix B

Using eq. (14), setting $g_i = 1$ for all $i = 1, 2, \ldots, M$ ($N_0 = M$ and all n_i are 0 or 1), and taking the p_i from eq. (15) (that is, eq. (A.1)) we get the generating function

$$G_N^*(s) = \sum_{n_1} \sum_{n_2} \cdots \sum_{n_M} p_1^{n_1} (1 - p_1)^{1 - n_1} s^{-n_1(n_2 w_{12}^* + n_3 w_{13}^* + \cdots + n_M w_{1M}^*)}$$

$$\times p_2^{n_2} (1 - p_2)^{1 - n_2} s^{-n_2(n_1 w_{21}^* + n_3 w_{23}^* + \cdots + n_M w_{2M}^*)} \cdots$$

$$\cdots p_M^{n_M} (1 - p_M)^{1 - n_M} s^{-n_M(n_1 w_{M1}^* + n_2 w_{M2}^* + \cdots + n_{M-1} w_{MM-1}^*)} \,, \tag{B.1}$$

with $s = s_N^{1/2} = \exp(1/2T^*)$. The terms with w_{ii} do not contribute to G_N^*. It is $n_1 + n_2 + \cdots + n_M = N$, $U_{i_j} = |\varepsilon| \, U_{i_j}^*$, and we find

$$G_N^*(s) = \sum_{i_1=1}^{M} \sum_{i_2=2}^{M} \cdots \sum_{i_N=N}^{M} P_{i_1} P_{i_2} \cdots P_{i_N} s^{-U_{i_1}^*} \cdots s^{-U_{i_N}^*},$$

$$i_1 < i_2 < \cdots < i_N, \tag{B.2}$$

where P_{i_j} is the probability that the sites $i_{j-1} + 1, i_{j-1} + 2, \ldots, i_j - 1$ are not occupied and the site i_j is occupied by by any particle. U_{i_j} is the potential energy of this particle and $U_{i_1} + U_{i_2} + \cdots + U_{i_N} = 2U_t$. Eq. (B.2) can be written in the form

$$G_N^*(s) = \sum_{i_1=1}^{M} \sum_{i_2=1}^{M} \cdots \sum_{i_N=1}^{M} \frac{1}{N!} P_{i_1} P_{i_2} \cdots P_{i_N} s^{-U_{i_1}^* - U_{i_2}^*} \cdots s^{-U_{i_N}^*}. \tag{B.3}$$

Thereby P_{i_j} is the probability that the sites $i_{k_{j-1}} + 1, i_{k_{j-1}} + 2, \ldots, i_{k_j} - 1$ are not occupied and the site $i_{k_j} = i_j$ is occupied by any particle. It is $i_{k_{j-1}} < i_{k_j}$ for all $k_j = 1, 2, \ldots, N$. Introducing $P_{i_j} = P_{i_j}^*[N - (j - 1)]$ one gets from eq. (B.3)

$$G_N^*(s) = \sum_{i_1=1}^{M} \sum_{i_2=1}^{M} \cdots \sum_{i_N=1}^{M} P_{i_1}^* P_{i_2}^* \cdots P_{i_N}^* s^{-U_{i_1}^* - U_{i_2}^*} \cdots s^{-U_{i_N}^*}, \tag{B.4}$$

where $P_{i_j}^*$ is the probability that the sites $i_{k_{j-1}} + 1, i_{k_{j-1}} + 2, \ldots, i_{k_j} - 1$ are not occupied and the site $i_{k_j} = i_j$ is occupied by the particle of number j. And this particle of number j has the potential energy U_{i_j}. Now we use conditional probabilities $P_j(U_j | U_{j-1} | \ldots | U_1) \, dU_j$, which are the probabilities that the particle of number j has the potential energy U_j in dU_j about U_j, if the particle of number 1 has the energy U_1, the particle of number 2 has the energy U_2, etc., and the particle of number $j - 1$ has the energy U_{j-1}. Thus, eq. (B.4) leads to the exact equation $(N/M = N/N_0 \ll 1)$

$$G_N^*(s) = \int \int \cdots \int \left(\prod_{j=1}^{N} [P_j(U_j | U_{j-1} | \cdots | U_1) \, s^{-U_j^*}] \right) dU_1 \ldots dU_N$$

$$= V^{-N} Q \tag{B.5}$$

with $U_j = |\varepsilon| U_j^*$. Eq. (B.5) is relation (20) in section 2.1 of our paper.

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