

STRUCTURES OF LIQUIDS WITH NON-CENTRAL INTERACTIONS

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Abstract - At present, two different methods are employed to take into account the structural contribution of non-central intermolecular interactions. The first is the perturbation method, which should work well at not too high densities; the second method tries to separate in an approximate way the configurational part and the orientational part of the partition function. The perturbation method can be varied by making different choices of the reference system and the perturbing potential, and some significant choices will be outlined. If the non-central part of the intermolecular interaction is a dipolar part only, the density dependence of the Kirkwood g -factor should be positive in first order perturbation. Structures like in fluid acetonitrile, where the density-dependence of the Kirkwood g -factor changes sign, can only be explained by a more complicated intermolecular interaction, or by the unknown higher order terms in the perturbation scheme.

The approximate factorization of the partition function into a configurational and an orientational part is less developed, but looks very promising, especially for getting insight into the behaviour of a liquid at high densities, up to triple point densities.

INTRODUCTION

Before treating liquids composed of molecules with non-central forces, let me briefly recapitulate the theory of central-force liquids. The main breakthrough of the last 15 years was the recognition that the structure of fluids at high density is solely determined by the repulsive branch of the intermolecular interaction (1-4). This is particularly true if long-range forces are absent, and if the division of the potential into a repulsive and an attractive branch is performed according to the suggestion of Weeks, Chandler and Andersen (3) (fig.1). One might visualize that the attractive branches of the potentials, which the neighbouring molecules exert on the central molecule, superpose to a homogeneous background potential (fig.2).

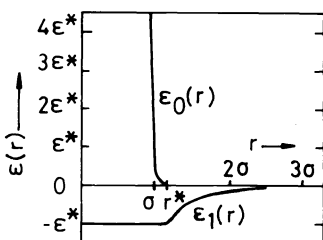


Fig. 1. Decomposition of a Lennard-Jones-type potential, $\epsilon(r)$, into a part representing only repulsive forces, $\epsilon_0(r)$, and a part representing all attractive forces $\epsilon_1(r)$, viz. $\epsilon(r) = \epsilon_0(r) + \epsilon_1(r)$. Thus: $\epsilon_0(r) = \epsilon(r) + \epsilon^*(r < r^*)$; $\epsilon_0(r) = 0 (r \geq r^*)$. $\epsilon_1(r) = -\epsilon^*(r < r^*)$; $\epsilon_1(r) = \epsilon(r) (r \geq r^*)$. (After Ref.3).

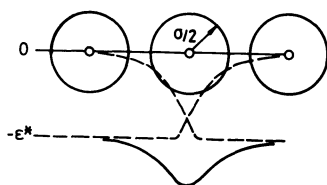


Fig. 2. Schematic representation of the influence of two neighbouring molecules on a central molecule (circles with radius $\sigma/2$) when only the attractive part of the potential in the Weeks-Chandler-Andersen decomposition is considered (broken curves). The particles are at somewhat larger distance than r^* . The corresponding background potential obtained by superposition is rather smooth (solid curve) with a shallow minimum at the position of the central molecule. In the three-dimensional multi-particle case, an increased smoothing effect ("smearing") is to be expected. (After Ref.4).

This attractive, homogeneous background potential is responsible for the cohesive energy, but has no influence on the structure, as no forces are exerted by it. In mathematical terms, the free energy is then given by the free energy F_0 of the assembly interacting with repulsive forces, plus a perturbation term taking into account the attractive potential ϵ_1 :

$$F = F_0 + \frac{N^2}{2V} \int_0^{\infty} \epsilon_1(r) g_0(r) 4\pi r^2 dr. \quad (1)$$

This simple possibility of calculating the free energy, called the High Temperature Approximation (as only the first perturbation term in a $1/T$ -expansion is involved) breaks down at low and intermediate densities, where the superposition of the potentials of the neighbouring molecules will not lead any more to a homogeneous background potential. But this will not concern us here. Attention should be called to the fact that the high temperature approximation corresponds closely to a generalized van der Waals model, the hard sphere term given by the term coming from the repulsive interactions, and the term $-A/V$ given by the perturbation term, where the "constant" A contains a slight density dependence from the pair distribution function. The question remains how to calculate the free energy of the assembly interacting by repulsive forces. One possibility is the standard method according to Weeks, Chandler, and Andersen, and elaborated by Verlet and Weis (5), by referring back to a hard sphere system. The second possibility is the explicit calculation on the basis of the softly repulsive potential. By a method invented by Baxter (6,7) it is very easy and quick to arrive at a Percus-Yevick solution for the pair distribution function of an assembly interacting with a potential of finite range. This way the pressure can be calculated for various densities, and by integration the free energy. For potentials where the repulsive branch is not much softer than that of a Lennard-Jones potential, the two methods lead to the same results. For very softly repulsive potentials, I believe that the Percus-Yevick method is preferable.

REFERENCE POTENTIALS FOR NON-CENTRAL INTERACTION

After this brief sketch I would like to proceed to the question how to take into account anisotropic intermolecular interaction. In the following I will confine myself to very simple examples, the interaction between linear molecules, and dipole-dipole interaction. The usual way is to treat the non-central force assembly by calculating the deviation from the properties of a suitable reference assembly, where the particles interact with central force potentials. It has been suggested also to go back to non-central force reference assemblies (8), but I will not refer to this. The central force reference assembly is constructed by a suitable angle-averaging procedure of the angle-dependent interaction potential. Two methods of this angle-averaging are of particular interest: The first uses as a reference potential the one coming from an unweighted averaging over the angles (9,10,11), the second performs the angle-averaging over the Boltzmann factor (12).

Thus, when the anisotropic potential is

$$\epsilon(R_{ij}, \omega_i, \omega_j), \quad (2)$$

method 1 uses

$$\langle \epsilon(R_{ij}, \omega_i, \omega_j) \rangle_{\omega_i, \omega_j}, \quad (2a)$$

while method 2 uses ϵ_{eff} , which is given by

$$e^{-\epsilon_{\text{eff}}/kT} = \langle e^{-\epsilon(R_{ij}, \omega_i, \omega_j)/kT} \rangle_{\omega_i, \omega_j}. \quad (2b)$$

The brackets $\langle \rangle$ are used to denote angle-averaging.

Before going into details, a brief qualitative discussion of the two methods might be in order. Let me consider the example of hard diatomics (hard dumbbells): it is clear that $\langle \epsilon \rangle$ is that of a hard sphere with the dimension of the long axis of the dumbbell, whereas ϵ_{eff} is a very softly repulsive potential (fig.3). This example shows immediately how the $\langle \epsilon \rangle$ is much more repulsive than the full angle-dependent potential; whereas one might suspect that ϵ_{eff} overdoes the weighing of the not-so-repulsive situations.

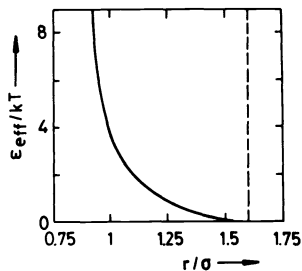


Fig. 3. Plot of ϵ_{eff}/kT vs. separation for a model of hard dumbbells with $l/\sigma = 0.6$ (l ..diatomic distance, σ ..diameter of one atom). The broken line indicates $\langle \epsilon \rangle$, which increases to infinity at the contact distance 1.6σ (After Ref.4).

This is confirmed by fig.4, which shows the residual free energy of Lennard-Jones diatomics with an anisotropy corresponding to the nitrogen molecule. The $\langle \epsilon \rangle$ curve is much too positive, whereas the ϵ_{eff} -curve deviates only at high densities from the calculations which agree ϵ_{eff} with computer simulations.

In spite of the obvious advantage of the ϵ_{eff} -reference assembly, which is much closer to the properties of the non- ϵ_{eff} central force assembly than the $\langle \epsilon \rangle$ -reference assembly, much more calculations have been carried out on the $\langle \epsilon \rangle$ -basis, and we will have to refer to this method as well. One should bear in mind, however, that as a consequence of the big differences between the properties of the true assembly and the $\langle \epsilon \rangle$ -reference assembly, simple first order corrections will not be able to account for these differences.

PERTURBATION THEORY

The perturbation method consists of introducing the perturbing term with a factor of λ ($\lambda=0$, if no perturbation is taking place, and $\lambda=1$, if the full perturbation is switched on), and developing the function in question into a Taylor series with respect to λ .

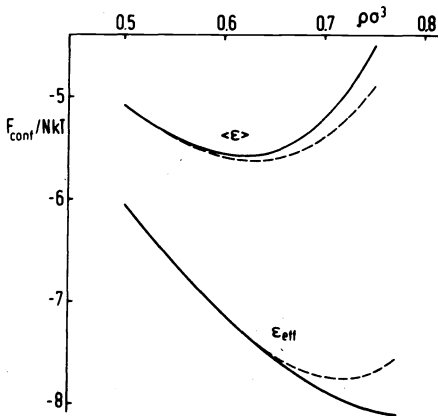


Fig. 4. The density dependence of the configurational free energy for Lennard-Jones diatomics with $1/\sigma = 0.33$. The full curves are for the $\langle \epsilon \rangle$ - and ϵ_{eff} -reference assembly, resp., the broken curves give orientational corrections dealt with later. The broken curve for ϵ_{eff} furnishes pressures which are close to computer simulation results (cf. fig. 12).

Finally, λ is set equal to unity.

Using method 1 for the reference potential, we have

$$\epsilon = \langle \epsilon \rangle + \lambda \epsilon_A, \quad (3)$$

which leads to the first non-zero correction term of the free energy (second order in λ):

$$\begin{aligned} \frac{F-F_0}{NkT} = & -\frac{\rho}{4} \left(\frac{1}{kT} \right)^2 \int_0^\infty g_0 \langle \epsilon_A^2 \rangle 4\pi r^2 dr \\ & - \frac{\rho^2}{2} \left(\frac{1}{kT} \right)^2 \int_0^\infty g_0^{(3)}(1,2,3) \langle \epsilon_A(1,2) \epsilon_A(2,3) \rangle_{1,2,3} dr_2 dr_3. \end{aligned} \quad (4)$$

Similarly, the first-order term for the angle-dependent pair correlation function is

$$g_1 = -\frac{\epsilon_A}{kT} g_0 - \frac{\rho}{kT} \int_0^\infty g_0^{(3)}(1,2,3) \langle \epsilon_A(1,3) + \epsilon_A(2,3) \rangle_3 dr_3. \quad (5)$$

Notice that part of the correction for the free energy goes linear with the particle density $\rho = N/V$, and is always negative. The second part, proportional to ρ^2 and involving the triplet correlation function, can be simplified for certain symmetries of the anisotropic part of the potential; e.g., it is zero for dipole-dipole interaction. The first-order approximation to the angle-dependent pair correlation function consists of one part, which is almost independent of density (a small density dependence is in g_0), and a second part, which is linear in ρ and involves the triplet correlation function. Again, this second part equals zero for dipole-dipole interaction.

Method 2 uses

$$\epsilon = \epsilon_{\text{eff}} - kT \ln [1 + \lambda f] \quad (6)$$

with

$$f = \exp\left(-\frac{\epsilon - \epsilon_{\text{eff}}}{kT}\right) - 1 \quad (7)$$

This leads to the first non-zero correction to the free energy (second order in λ)

$$\frac{F-F_0}{NkT} = -\frac{\rho^2}{2} \int_0^\infty g_0^{(3)}(1,2,3) \langle f(1,2)f(2,3) \rangle_{1,2,3} d\mathbf{r}_2 d\mathbf{r}_3 \quad (8)$$

and to the first-order angle-dependent part of the pair correlation function

$$g_1 = f g_0 + \rho \int_0^\infty g_0^{(3)}(1,2,3) \langle f(1,3)+f(2,3) \rangle_3 d\mathbf{r}_3 \quad (9)$$

The structure of the formula for g_1 is quite similar to that derived by method 1. But the correction term for the free energy contains no part linear in density. This indicates already that method 2 takes more characteristic properties into the reference system than method 1.

DIPOLAR LIQUIDS (13)

Here I will confine myself to hard spheres or hard dumbbells with superimposed dipole moment. The potential for the dipole-dipole interaction is

$$\begin{aligned} \epsilon_{\text{dd}} &= -\frac{\mu^2}{r^3} [2\cos\theta_1 \cos\theta_2 - \sin\theta_1 \sin\theta_2 \cos(\phi_1 - \phi_2)] \\ &= -\frac{\mu^2}{r^3} D \quad (10) \end{aligned}$$

where D is an abbreviation for the combination of orientational coordinates. The angles θ_1 and θ_2 are between the dipole axis and the vector \mathbf{r} connecting the molecular centers, the angle $(\phi_1 - \phi_2)$ indicates how much molecule 2 is turned out of the plane formed by dipole axis 1 and vector \mathbf{r} . Another important combination of orientational coordinates determines the cosine of the angle between the dipole axes.

$$\cos\theta_{12} = \cos\theta_1 \cos\theta_2 + \sin\theta_1 \sin\theta_2 \cos(\phi_1 - \phi_2) = \Delta \quad (11)$$

The coefficient of the pair correlation function for this combination Δ determines the deviation of the Kirkwood g -factor (denoted by g_k) from unity:

$$g_k = 1 + \frac{\rho}{3} \int_0^\infty h_\Delta(r) 4\pi r^2 dr \quad (12)$$

Let us note some consequences of first-order perturbation theory for dipolar hard spheres. With the $\langle \epsilon \rangle$ -reference assembly,

$$\langle \epsilon \rangle = \epsilon_{\text{HS}} \quad (13)$$

$$\epsilon_D = -\frac{\mu^2}{r^3} \quad (14)$$

$$\epsilon_\Delta = 0 \quad (15)$$

As h_D and h_Δ are given by $-\epsilon_D g_{HS}/kT$ or $-\epsilon_\Delta g_{HS}/kT$, the Kirkwood g -factor cannot deviate from unity. With the ϵ_{eff} -reference assembly, the angle-averaged pair correlation function g_O^{eff} is almost identical with g_{HS} (except very high dipole moments), but the f_D and f_Δ are now for not too big dipole moments given by

$$f_D = \frac{\mu^2}{r^3 kT} - 0.0933 \left(\frac{\mu^2}{r^3 kT} \right)^3 + \dots \tag{16}$$

$$f_\Delta = 0.0801 \left(\frac{\mu^2}{r^3 kT} \right)^3 + \dots \tag{17}$$

Thus, f_Δ is very short ranged and positive. This gives a positive density-dependence on g_k , which goes faster than linear with ρ , as g_O peaks up in the short range with increasing density. It should be mentioned that first-order perturbation theory predicts a behaviour of h_D and h_Δ different to computer simulation (14) (fig.5).

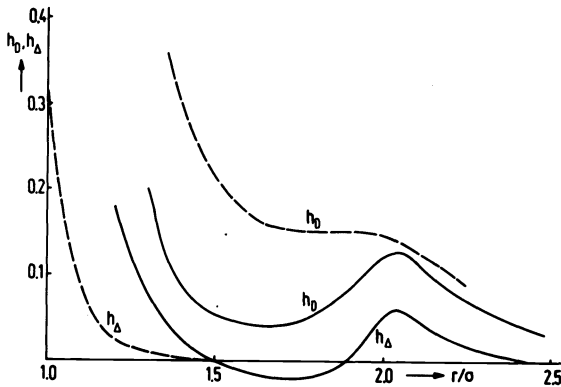


Fig. 5. The angular pair correlation functions h_D and h_Δ for hard sphere dipoles, according to first-order perturbation (broken curves), and according to linearized hypernetted chain theory (full curves), which agrees with simulation results extrapolated for an untruncated potential (14), for $\rho\sigma^3 = 0.8$ and $\mu^2/(\sigma^3 kT) = 1.0$.

Whether this has to do with the contribution of higher order terms (which are not separated from the first-order terms in the computer simulation) or with difficulties in the computer calculations, that is not yet definitely settled. The same difficulties appear, when a full numerical integration is used for the calculation of f_D and f_Δ , which is necessary for large dipole moments (fig.6). Another remark concerns the dependence of the Kirkwood g -factor on dipole moment at given density. Table 1 compares g_k according to

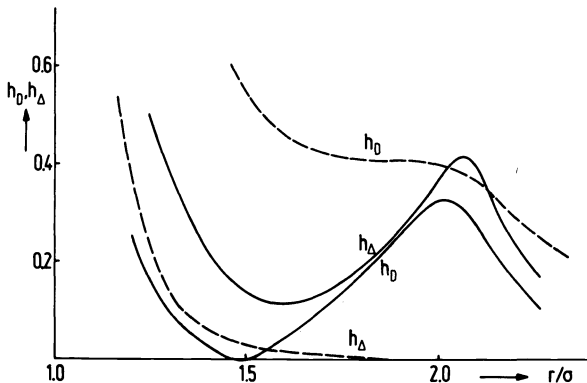


Fig. 6. As fig.5, but for $\mu^2/(\sigma^3 kT) = 2.75$.

the first-order expansion with results from the linearized hypernetted chain theory (14). For low dipole moments the first-order perturbation method gives g_k -values much nearer to unity. Again, the reason for this disagreement is hard to trace back.

TABLE 1. The Kirkwood g -factor for $\rho\sigma^3 = 0.8$ with respect to the dipole moment for hard sphere dipoles, calculated by linearized hypernetted chain theory and first-order perturbation, resp..

$\frac{\mu^2}{\sigma^3 kT}$	L.H.N.C. g_k	1 st -order pert. g_k
0.00	1.00	1.00
0.25	1.10	1.00
0.5	1.24	1.01
0.667	1.43	1.03
1.0	1.81	1.10

Most interesting is the extension to dipolar hard dumbbells on the basis of the ϵ_{eff} -reference assembly. The hard dumbbell ϵ_{eff} is not appreciably modified by the superposition of the dipole-dipole interaction, so g_0 can be taken as that of hard dumbbell assemblies (except for very big dipole moments). Very dramatic is the change in f_{Δ} , which has to be calculated by a numerical integration procedure. Outside the range of ϵ_{eff} , that is at distances $r \geq 1 + \sigma$ (l being the diatomic distance, and σ the diameter of one atom), f_{Δ} is identical with that in case of dipolar hard spheres. But for distances $\sigma \leq r \leq 1 + \sigma$, f_{Δ} turns to negative values (fig.7). Therefore, for sufficiently large l/σ and densities where g_0 has a pronounced peak in this short range, g_k will have a negative density dependence. In fig. 8 and fig. 9, the density dependence for g_0 and h_{Δ} is shown for $l/\sigma = 0.6$.

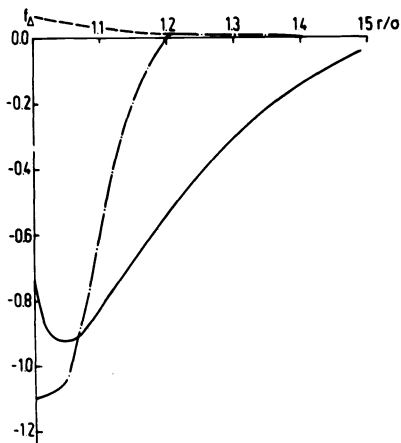


Fig. 7. The coefficient f_{Δ} for $\mu^2/(\sigma^3 kT) = 1.0$, for dipoles superimposed on hard spheres (broken curve), hard dumbbells with $l/\sigma = 0.2$ (dash-dotted curve), and hard dumbbells with $l/\sigma = 0.6$ (full curve).

It is clear, that the negative density dependence of g_k becomes much more pronounced at high densities. Thus, the density dependence of g_k , found experimentally on HCl and CH_3CN (15) (fig.10), corresponds qualitatively to the predictions for dipolar hard spheres, and dipolar hard dumbbells, resp.. One might visualize this result by "turning on" a dipole moment in a hard sphere or hard dumbbell assembly. In the hard sphere assembly, the dipole moments will orientate on line, that is in the electrostatically most favourable orientation. In the hard dumbbell assembly, the dipole moments can get near one another only in less favourable orientations, which are more or less antiparallel.

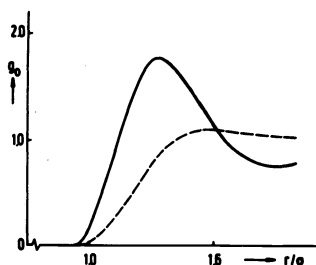


Fig. 8. Pair correlation function for hard dumbbells ($l/\sigma = 0.6$) interacting with ϵ_{eff} , for $\rho\sigma^3 = 0.07$ (broken curve) and $\rho\sigma^3 = 0.466$ (full curve).

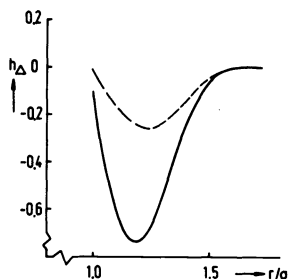


Fig. 9. The angular pair correlation function h_A for hard dumbbells ($l/\sigma = 0.6$) with dipole moment ($\mu^2/(\sigma^3 kT) = 1.0$), for $\rho\sigma^3 = 0.07$ (broken curve) and $\rho\sigma^3 = 0.466$ (full curve).

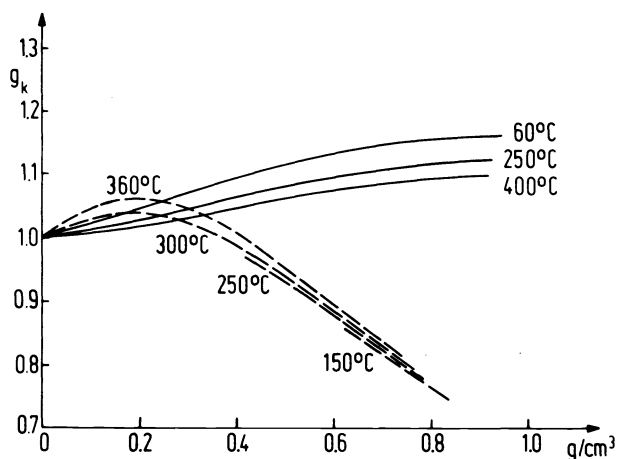


Fig. 10. The density dependence of the Kirkwood g -factor of HCl (full curve) and CH_3CN (15) (broken curve).

SEPARATION OF ORIENTATIONAL PARTITION FUNCTION AT HIGH DENSITIES

In the perturbation theory, difficulties are met when the perturbation has to be carried to higher order. Already the first non-zero terms involve in the general case the triplet correlation function. A noticeable exception is the treatment of Gubbins et al. (16) for multipole potentials, which uses two terms in the free energy perturbation expansion and approximates more by use of a Padé approximant. But in general it is fair to say that perturbation methods will break down at high densities for large perturbing terms, as, e.g., in the case of anisotropic shape of the molecules. Here another method of separating the positional and orientational part of the partition function has been developed recently. A move was made by Beret and Prausnitz (17), still carrying empirical features, which was interpreted in the above sense by the author (18). A much better founded treatment was given lately by Fischer (19).

The essential idea is as follows:

In the configurational integral

$$Q' = \int \exp \left\{ -\frac{1}{kT} \sum_{i < k} \varepsilon(r_{ik}, \omega_i, \omega_k) \right\} d\underline{r}_1 \dots d\underline{r}_N d\omega_1 \dots d\omega_N, \quad (18)$$

let us first split the potential into an angle-independent ε_s and an anisotropic part $\varepsilon_A = \varepsilon - \varepsilon_s$:

$$\begin{aligned} Q' &= \int \exp \left\{ -\frac{1}{kT} \sum \varepsilon_s(r_{ik}) \right\} d\underline{r}_1 \dots d\underline{r}_N \\ &\times \int \exp \left\{ -\frac{1}{kT} \sum \varepsilon_A(r_{ik}, \omega_i, \omega_k) \right\} d\omega_1 \dots d\omega_N \\ &= Q'_r \cdot Q'_\omega \quad . \end{aligned} \quad (19)$$

In Q'_r , there will be some configurations contributing strongly to the integral and many others with almost vanishing contribution. The evaluation of Q'_ω is only necessary for those configurations contributing significantly to Q'_r . Let us call one typical important configuration $\{r_1^0, \dots, r_N^0\}$. The essential assumption is now that $Q'_\omega(\underline{r}_1, \dots, \underline{r}_N)$ is nearly equal for all the important configurations.

This yields for the configurational integral

$$Q' = Q'_r \cdot Q'_\omega(r_1^0, \dots, r_N^0) \quad , \quad (20)$$

where the orientational part is evaluated only for one important configuration. This configuration is taken as the cubic dense packing. Thus the configurational integral is split into that of a spherical assembly and a density-dependent function, which is constructed from the orientational integral of a face centered cubic lattice.

I will not go into the details of Fischer's evaluation of the orientational integral, but would like to point out that at the price of some reasonable additional assumptions the evaluation could be done in an extremely quick way. It seems to me that this method can beat every other in speed and also accuracy, if the density is sufficiently high. For lower densities, the regular lattice is not a good choice for the typical important configuration, and it is clear, that the orientational contribution will be too small in that case. As illustration the method has been applied to an assembly of Lennard-Jones diatomics with potential parameters corresponding to nitrogen. The result is shown in fig.4 for the free energy along one isotherm. The orientational correction to the ε_{eff} -curve for the free energy furnishes pressures (fig.11), which are in ε_{eff} reasonable agreement to molecular dynamics results (20,21). Without that correction, a reasonable calculation of the zero-pressure density (i.e. the density of the liquid under its vapour pressure) would be impossible. It is of interest that even at the zero-pressure density most contributions to the orientational integral come from differences in the attractive part of the potential. Therefore, it is understandable, that with a worse choice of the spherical reference potential the orientational correction would be too small, as is demonstrated on the $\langle \varepsilon \rangle$ -reference assembly. It should be noted also that the density dependence of the correction is very strong, much stronger than with ρ or ρ^2 as first-order perturbation demands.

Though one should await the extension of this method to molecules of bigger anisotropy and perhaps also polar molecules, it seems that we have now a powerful tool in our hands for the region of high densities, where the application of perturbation methods becomes doubtful.

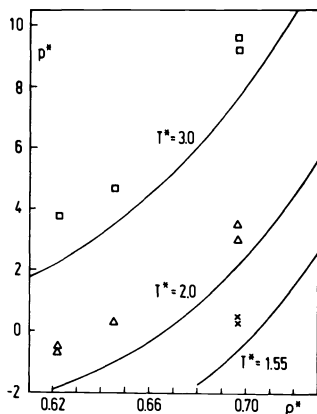


Fig. 11. Reduced pressure $p^* = p\sigma^3/\epsilon^*$ vs. reduced density $\rho^* = \rho\sigma^3$, for three isotherms $T^* = kT/\epsilon^* = 1.55, 2.0$ and 3.0 . Full curves are on the basis of an ϵ_{eff} -reference assembly with Fischer's orientational correction, points are molecular dynamics results (20,21). After Ref. 19.

CONCLUSION

We are still at the beginning of an insight into the structure and thermodynamic properties of molecular fluids. I have not mentioned at all our ignorance about real interaction potentials. It is for this ignorance, that I have presented properties of model liquids and only vaguely indicated the bearing on real liquids.

In the statistical-mechanical treatment of molecular fluids the introduction of the ϵ_{eff} -reference potential is, in my opinion, of fundamental importance, as was the splitting of the potential into a repulsive and attractive branch according to Weeks, Chandler, and Andersen for central-force liquids. But it is clear now that even with the ϵ_{eff} -reference assembly, thermodynamic properties and structural features depend strongly on orientational correction terms. For not too high densities, first-order perturbation is applicable. For high densities, a new method consisting of a separation of a strongly density-dependent orientational factor out of the configurational integral seems to be very promising.

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