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A MODIFIED CELL THEORY OF THE LIQUID STATE

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A generalization of lattice-cell theories of liquids is proposed by introduction of a structure of cells of different size. The number of molecules contained in cells with a radius r is determined by a function $f_c(r)$ describing essentially the collision probability of two particles. A relation between $f_c(r)$ and the radial distribution function $g(r)$ is given. Any regular (lattice-like) arrangement of the molecules is not supposed. The estimation of thermodynamic quantities is shown both in a semiclassical approximation and in a quantum-statistical version. Particularly we studied the equation of state of simple liquids (neon, methane). Correlations are found between the shape of the distribution $f_c(r)$ and the course of the equation of state. The theory gives the usual cell theory behaviour and additionally some interesting new features.

1. Introduction

The proposed theory is in an extension and modification of well-known lattice-cell models of simple liquids with regard to a more realistic description of the liquid structure. The conventional cell theories[1]) (for instance the Lennard–Jones Devonshire theory) assume a regular (lattice-like) arrangement of particles enclosed in cells consisting of the next neighbour molecules.

Analyzing the radial distribution function (RDF)[2,3]) of liquids we notice that these assumptions lead to an inadequate picture of the molecular structure of the liquid state.

The RDF shows that the probability to find a neighbouring particle of any molecule in the liquid is smeared over a finite range of distances. Thus the supposition of a regular arrangement of molecules with fixed distances (lattice) and the idea to localize all molecules of the liquid in cells of the same shape and size are to be regarded as a drastic simplification of the real structural situation in liquids.

In order to overcome these imperfections in the description of the liquid structure a lot of attempts are made.

Of special interest in our connection are investigations of quasi-lattice structures to restrict long-range order effects. Franchetti[4]) proposed such a quasi-lattice model and showed the way to estimate the RDF.

Recently Baer[5]) investigated structural correlations by means of a "structural diffusion" model based on a local lattice structure with spatially varying lattice parameters using some well-known ideas of Prins[6]) and Frenkel[7]).

Hoover et al.[8]), analyzing computer simulations, suggested an improvement of the cell theory by the introduction of cells with different sizes and shapes.

In first respect the mentioned models are to be regarded as contributions to a satisfactory picture of the liquid structure. But in almost all cases the development of the theories is not yet suitable for the calculation of thermodynamic quantities of concrete systems. We have developed a modified cell theory (MCT), which allows both a detailed representation of the liquid structure by means of a generalized cell model and the estimation of the thermodynamic behaviour.

In agreement with structural data[2,3]) we suppose a distribution of different distances between neighbouring particles in the liquid. In terms of a cell theory that means: We have to distribute the molecules over cells of different sizes. The averaged cell volume in this structure is equal to the volume of the elementary cell in conventional lattice cell theories. This technique is similar to the quoted suggestions of Hoover et al.[8]) to improve the cell theory.

On the basis of our model we have calculated thermodynamic quantities not only in a semiclassical but also in an exact quantum-statistical manner.

2. Characteristics of the model

We assume that all particles of the system are contained in (approximately) spherical cells with exactly one molecule in one cell. The number of cells is supposed to be equal to the number of particles. Contrary to the conventional cell theories, using a fixed cell radius, we introduce in the MCT a distribution of different cell radii $f_c(r)$. This distribution determines the part dN_{r_c} of the total number of molecules N enclosed in cells with a radius between r_c and $r_c + dr$.

Then dN_{r_c} may be given by

$$dN_{r_c} = N f_c(r_c)\, dr, \tag{1}$$

with the normalizing condition

$$\int_0^\infty f_c(r)\, dr = 1. \tag{2}$$

In order to relate the distribution of cell sizes to the volume of the liquid we formally define an averaged cell radius $\bar{r}_c$:

$$\bar{r}_c = \int_0^\infty r f_c(r)\, \mathrm{d}r. \tag{3}$$

Then in close analogy to the usual cell theories we express the volume V of the liquid by

$$V = \alpha \bar{r}_c^3 N. \tag{4}$$

It is important to emphasize that eqs. (3) and (4) do not imply the introduction of any lattice-like arrangement of the particles with a lattice constant $\bar{r}_c$. These relations serve to (approximately) estimate the volume of the model structure consisting of a distribution of cells of different sizes according to a given function $f_c(r)$. The averaged cell radius $\bar{r}_c$ has – contrary to $f_c(r)$ – only the meaning of a formal mathematical quantity without any physical relevance.

The parameter α in eq. (4) gives the density of package of fictitious spheres with a diameter $\bar{r}_c$. For instance we have $\alpha = 1/\sqrt{2}$ in a regular close-packed structure.

The main problem of the structural description on the basis of this model remains the determination of the distribution of cell radii $f_c(r)$. This function should reflect the most important features of the liquid structure, especially the results of scattering experiments.

To reach this aim we have to relate the distribution $f_c(r)$ to the (experimentally established) RDF $g(r)$ of the liquid[2,3]). It is plausible to define the magnitude of a cell, containing a particle, by the distance ("free path") which this molecule moves before it collides with a neighbouring particle. Precisely spoken we suppose that the part $\mathrm{d}N_{r_c}$ of the total number of particles N colliding *for the first time* with another molecule in a distance range between r_c and $r_c + \mathrm{d}r$ may be enclosed in cells with the radius r_c. If we remember the definition of the RDF[9]) we can write down the number density in a distance r (i.e. the density in a spherical cell with the radius r and the thickness $\mathrm{d}r$):

$$\rho(r) = \rho g(r). \tag{5}$$

The number density on the surface of a sphere with the radius r_c is then given by

$$\rho(r_c)\, \mathrm{d}r = \rho g(r_c)\, \mathrm{d}r. \tag{6}$$

Now it is reasonable to choose the probability of collision between two particles in a distance r_c as proportional to the density eq. (6). The part $\mathrm{d}N_{r_c}$ of molecules colliding in a distance r_c for the first time with a neighbouring particle is now to be regarded as proportional to the just mentioned probability of finding a second particle in a distance r_c. Furthermore the quantity dN_{r_c} may be supposed as proportional to the number of molecules $N(0, r_c)$, penetrating a distance $0 \ldots r_c$ into the shell consisting of the neighbouring particles without a collision. So we obtain:

$$dN_{r_c} = C\rho N(0, r_c) g(r_c)\, dr. \tag{7}$$

In order to estimate the quantity $N(0, r_c)$ we assume that the number of particles moving a finite distance without a collision will decrease proportional to the corresponding number density $\rho(r)$ given by eq. (5). In this case we can easily derive:

$$N(0, r_c) = N \exp\left\{-\lambda\rho \int_0^{r_c} g(r)\, dr\right\}. \tag{8}$$

Combining both relations (7) and (8) the number dN_{r_c} is finally

$$dN_{r_c} = C\rho N g(r_c) \exp\left\{-\lambda\rho \int_0^{r_c} g(r)\, dr\right\}. \tag{9}$$

Now the distribution function $f_c(r)$ is given by a comparison between eqs. (9) and (1) as

$$f_c(r) = C\rho g(r) \exp\left\{-\lambda\rho \int_0^{r} g(r')\, dr'\right\}. \tag{10}$$

Eq. (10) is the desired relation between the (experimentally accessible) RDF of the liquid and the distribution of molecules over cells of different sizes in the MCT.

But the attempt to use eq. (10) directly for a calculation of $f_c(r)$ leads to some difficulties.

The most serious problem consists in an insufficient accuracy of experimentally obtained RDF's of real liquids. This is evident if we remember that the use of eq. (10) requires the knowledge of $g(r)$ depending on the density and the temperature of the liquid.

Until now the most detailed X-ray study of the structure of liquid argon is made by Micolaj and Pings^2). Even this extensive work only leads to RDF's of some selected thermodynamic states and these data do not permit the establishment of $g(r)$ as a function of ρ and T. An application of eq. (10) is also limited by the numerical amount of calculations rapidly increasing with the use of more detailed expressions for $g(r)$.

So first of all the importance of eq. (10) does not consist in a direct estimation of the distribution $f_c(r)$; but employing this relation it is possible to

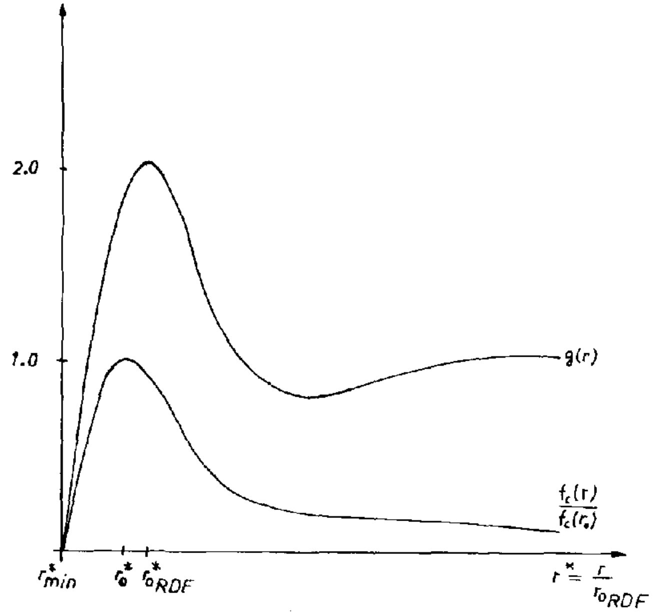

Fig. 1. Radial distribution function $g(r)$ – closely related to ref. 2 – and corresponding cell size distribution $f_c(r)$ obtained by eq. (10).

establish a reasonable ansatz for $f_c(r)$. We regard a model of $g(r)$ (given in fig. 1) closely related to the quoted results of Mikolaj and Pings[2]). By numerical integration of eq. (10) we obtain the corresponding cell size distribution $f_c(r)$ (fig. 1).

The main features of this function are:

(1) In the range $r \leqslant r_0$ is (approximately):

$$g(r) \propto f_c(\mathrm{r}),$$

representing, that in this region the probability to collide with a molecule for the first time is (approximately) equal to the probability to collide with any molecule of the system at all.

(2) The maximum is situated in the neighbourhood of the position $r_{0_{\mathrm{RDF}}}$ of the mean peak of $g(r)$.

(3) For large r an exponential decrease is found. (Generally this result follows from eq. (10) assuming $g(r) \approx 1$ for $r \gg r_0$).

A representation of such a type of functions is possible by the aid of the well-known Γ-distribution[10]):

$$f_c(x) = \frac{1}{\Gamma(s)} \left(\frac{s-1}{x_0}\right)^s x^{s-1} \exp\left\{-(s-1)\frac{x}{x_0}\right\}, \tag{11}$$

with the parameters x_0 (position of the maximum of $f_c(x)$) and s. The behaviour of the Γ-distribution by variation of s is shown in fig. 2.

Defining the quantity x by

$$x \equiv r - r_{\min}, \tag{12}$$

we can regard eq. (11) as an expression for the cell size distribution. A comparison of fig. 2 with fig. 1 directly shows the representation of the main features of $f_c(r)$ by means of the Γ-distribution.

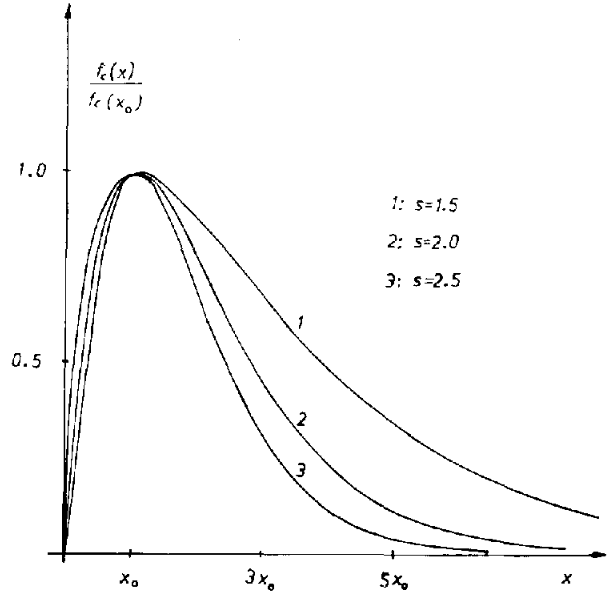

Fig. 2. Γ-distribution eq. (11) as a model of the cell size, distribution $f_c(x)$.

In order to illustrate the superiority of our structural description compared with conventional lattice-cell models we emphasize the more realistic representation of density variations by means of the MCT.

Changes in the liquid volume are realized in the usual cell theories by a variation of the lattice constant (i.e. a change of the next neighbour distance). This however disagrees completely with experimental results. It is well known from structural investigations of simple liquids[2,3]) that the distance of next neighbours – represented by the position of the main peak of the RDF – is (almost) constant over a wide range of densities. The variation of the volume is essentially due to a change of the next neighbour number.

The description of density variations in terms of the MCT represents the experimental observed constancy of the first peak of the RDF (i.e. the constancy of next neighbour distances) by a constant position of the maximum of the distribution $f_c(r)$.

The variation of next neighbour numbers is realized by an appropriate change of the distribution of the molecules over different cell sizes.

3. Formal development of the theory

In order to estimate the thermodynamic properties of liquids on the basis of the proposed structural model we have to write down the partition function of the system.

Generally this is a serious problem. But using the approximation of independent motion of the particles in their cells (analogous to most of the conventional lattice-cell models[1]), the partition function of the system Z is given by a product of partition functions Z_{r_i} of single molecules contained in cells with the radius r_i:

$$\ln Z = \sum_i N_{r_i} \ln Z_{r_i}. \tag{13}$$

The quantity N_{r_i} is the number of particles enclosed in cells with the radius r_i supposing in the model only a discrete sequence of cell radii with constant differences ϵ:

$$r_{i-1} - r_i = \epsilon. \tag{14}$$

For $\epsilon \to 0$ the number N_{r_i} goes over in the quantity $\mathrm{d}N_{r_i}$ of eq. (1). We can neglect the error of the approximation of discrete cell radii eq. (14) by an appropriate choice of ϵ; i.e. the magnitude of ϵ is to be chosen small enough.

The thermodynamic properties are determined by the partition function of the liquid versus temperature T and volume V [11]). A simplification is given by the use of experimentally obtained structural characteristics of simple liquids. It is found[2,3]) that the liquid structure above all depends on the density of the system but relatively little on the temperature (of course only by variation of temperature and volume within the limitations of the liquid phase of the investigated substance).

On the other hand the behaviour of particles in cells of given size (i.e. the behaviour of the quantities Z_{r_i}) should be determined only by the temperature. This leads to the following relation for the partition function:

$$\ln Z = \ln Z(T, V) = \sum_i N_{r_i}(V) \ln Z_{r_i}(T). \tag{15}$$

The free energy of the system is then given by

$$F(T, V) = -kT \ln Z(T, V) = -kT \sum_i N_{r_i}(V) \ln Z_{r_i}(T). \tag{16}$$

The other thermodynamic quantities follow from eq. (16) by differentiation with respect to T and V. We obtain the temperature derivatives of eq. (16) essentially by differentiation of the "cell partition functions" Z_{r_i} with respect to T. This is almost the same procedure as in conventional lattice-cell theories. We assume in analogy to these models that the particles may move in their cells within a cell field (for instance within the Lennard-Jones–Devonshire cell potential[1]). The difference to the cell theories with a fixed cell size is: In the MCT we have to calculate a set of partition functions Z_{r_i} including the derivatives $\partial Z_{r_i}/\partial T$, $\partial^2 Z_{r_i}/\partial T^2$ for the different cell radii occurring in the model. Because of the close relationship to the procedure in the usual cell theories we will not discuss here in detail the estimation of the quantities Z_{r_i}. In section 4 we present for a special cell field the practical calculation of the cell partition function and their derivatives with respect to T.

Now let us regard the volume dependence of the partition function given by a volume dependence of the particle numbers N_{r_i}. Here the approach is quite different from the treatment in usual cell theories because of replacing the variation of the lattice constant by a change of the cell size distribution $f_c(r)$. To determine the thermodynamic behaviour we have also to differentiate the partition function eq. (16) with respect to V:

$$\frac{\partial \ln Z}{\partial V} = \sum_i \ln Z_{r_i}(T) \frac{\mathrm{d}}{\mathrm{d}V} N_{r_i}(V), \tag{17}$$

i.e. we have to calculate the volume derivative of the numbers N_{r_i}. These are given by (compare with eq. (1)):

$$N_{r_i} = N \int_{x_i-\epsilon/2}^{x_i+\epsilon/2} f_c(x)\,\mathrm{d}x \approx N f_c(x_i)\epsilon. \tag{18}$$

If we apply the Γ-distribution eq. (11) to represent the distribution $f_c(r)$ we obtain:

$$N_{r_i} = \frac{N\epsilon}{\Gamma(s)} \left(\frac{s-1}{x_0}\right)^s x_i^{s-1} \exp\{-(s-1)x_i/x_0\}. \tag{19}$$

In order to describe the volume dependence of the quantities N_{r_i} we use the free parameters x_0 and s. The quantity x_0 gives the position of the maximum of $f_c(r)$ (compare section 2) and therefore x_0 should be independent of the volume. So we have to assume that only the parameter s depends on the liquid volume. To get an explicit expression for the relation $s(V)$ we employ eq. (3). For the Γ-distribution we find

$$\bar{r}_c = \frac{r_0 s - r_{\min}}{s - 1}, \tag{20}$$

and with eq. (4) we obtain

$$s(V) = \frac{1 - r_{\min}(\alpha N/V)^{1/3}}{1 - r_0(\alpha N/V)^{1/3}}. \tag{21}$$

Eqs. (19) and (21) give the volume dependence of the numbers $N_{r_i} = N_{r_i}(V)$. The distribution function $f_c(r)$ depends on the volume only implicitly through the parameter s. So we get the volume derivative of N_{r_i} in the following way:

$$\frac{\mathrm{d}N_{r_i}}{\mathrm{d}V} = \left(\frac{\mathrm{d}}{\mathrm{d}s} N_{r_i}(s)\right) \frac{\mathrm{d}s(V)}{\mathrm{d}V}. \tag{22}$$

By differentiation of eq. (19) with respect to s we obtain

$$\frac{\mathrm{d}}{\mathrm{d}s} N_{r_i}(s) = N_{r_i}(s) \left\{ \ln \frac{x_i}{x_0}(s-1) - \frac{x_i}{x_0} + \frac{s}{s-1} - \frac{\mathrm{d}}{\mathrm{d}s} \ln \Gamma(s) \right\}. \tag{23}$$

The derivation of eq. (21) with respect to the volume is given by

$$\frac{\mathrm{d}}{\mathrm{d}V} s(V) = \tfrac{1}{3}\left(\frac{\alpha N}{V^4}\right)^{1/3} \frac{r_{\min} - r_0}{[1 - r_0(\alpha N/V)^{1/3}]^2}. \tag{24}$$

Introducing eqs. (23) and (24) into the relation (22) the volume derivatives of the numbers N_{r_i} (i.e. the volume derivative of the partition function) are completely determined.

Up to now we have written down the basic relations for the estimation of the thermodynamic behaviour of a liquid by the aid of the MCT. For the practical calculations we have to choose only an expression for the cell field in which the particles move (see next section).

4. Calculations and results

For the calculation of thermodynamic properties of liquids we use as a first approximation a simple model of the force field in the cells. This cell potential $w_i(r)$, "felt" by a molecule in a cell with a radius r_i, may be given by

$$w_i(r) = \begin{cases} 0 & \text{for } r < r_i - r_d \\ \infty & \text{for } r \geq r_i - r_d, \end{cases} \tag{25}$$

where r is the distance from the centre of the cell and r_d is the particle diameter.

As interpretation of the cell field eq. (25) in terms of the well-known Lennard-Jones–Devonshire cell theory we can regard our expression (25) as a hard sphere approximation of the general Lennard-Jones–Devonshire cell potential.

By means of eq. (25) it is possible to carry out both the semi-classical and the quantum-statistical treatment of the theory with a justifiable amount of calculations. In the semiclassical approximation we can write down a simple analytic expression for the cell partition functions $Z_{r_i}(T)$:

$$Z_{r_i}(T) = \left(\frac{mkT}{2\pi\hbar^2}\right)^{3/2} \frac{4\pi}{3} (r_i - r_d)^3. \tag{26}$$

In eq. (26) m is the molecular mass, $\hbar$ means Planck's constant $\hbar = h/2\pi$, k is Boltzmann's constant. The temperature derivatives of the partition functions Z_{r_i} are directly obtained from eq. (26). A quantum-theoretical treatment requires the solution of the eigenvalue problem of the radial Schrödinger equation for the cell potentials $w_i(r)$ given by eq. (25). We obtain the following spectrum of energy levels[12]):

$$E_{ln}(r_i) = \frac{\hbar^2 \chi_{ln}}{2m} \frac{1}{(r_i - r_d)^2} \tag{27}$$

with the quantum numbers $l = 0, 1, 2, \ldots$ and $n = 1, 2, 3 \ldots$. The quantities χ_{ln} are the zeros of the spherical Bessel functions. Important for the practical calculations is the following fact: We have to determine the spectrum of the zeros χ_{ln} only once and then we get the energy eigenvalues for the different cell sizes directly by the simple relation (27).

Nevertheless the quantum-statistical partition functions

$$Z_{r_i} = \sum_{l,n} \omega_l \, e^{-E_{ln}/kT} \tag{28}$$

and the corresponding temperature derivatives are to be calculated numerically.

For the practical treatment of the MCT we have established an extensive computer program. This FORTRAN-program allows the estimation of thermodynamic quantities both in dependence of the temperature and of the density (the volume) of the liquid not only in the semiclassical but also in the quantumstatistical formulation of the theory. Putting in the necessary molecular data of the considered liquid as well as the model parameters of the theory it is possible to obtain the desired thermodynamic functions versus T and ρ in only one run of the computer. A detailed description of the numerical technique is given in [13]). On the basis of that program we have studied the thermodynamic behaviour of a number of simple liquids particularly liquid neon and liquid methane.

These estimations are model calculations in order to demonstrate the principle possibilities of the MCT compared with conventional cell theories.

For this reason we did not fit the used model parameters to experimental thermodynamic data. We only roughly adjusted these quantities to the experimentally accessible density range of the investigated liquid. The starting point for a determination of the input parameters is the maximum number density of the model structure fixing the position r_0 of the maximum of the cell size distribution:

$$\rho_{\max} = \frac{1}{\alpha r_0^3}. \tag{29}$$

This follows from eq. (4) introducing eq. (20) for the averaged cell radius r in case $s \to \infty$ (i.e. the transition to the minimum volume). For liquid neon we took the density range including the maximum density from experimentally PVT-data[17]) and by means of eq. (29) we estimated a value of $r_0 \approx 32.1$ nm.

For methane we used a value of $r_0 \approx 41.9$ nm introduced by Bhatia[18]) in a similar structural model.

Generally we did not vary this quantity but – in agreement with the basic ideas of the MCT – we assumed a fixed volume independent value for r_0 representing the experimentally found relative constancy of the nearest neighbour distance.

A comparison of the position of the main peak of the RDF and the maximum of the cell size distribution estimated by eq. (29) shows the required approximately agreement. (For neon using the structural data[3]) the accuracy is about 3%.)

For the particle diameter we took the values of the σ-parameter from the Lennard-Jones (6, 12)-potential[19]) varying this quantity in a range approximately corresponding to the accuracy of the experimental determination of σ (compare ref. 19).

A maximum for $r_0 - r_{\min}$ (i.e. a minimum for $r_{\min}$) is given by the difference $r_{0\mathrm{RDF}} - r_{\min\,\mathrm{RDF}}$ taken from RDF-data (compare eq. (10) and fig. 1) or approximately taken from a corresponding Lennard-Jones (6, 12)-potential in the form $2^{1/6}\sigma - \sigma$.

In order to investigate the temperature dependence of thermodynamic properties we have calculated the free energy F, the internal energy U, the entropy S, the heat capacity C_v as well as the pressure p versus T. In case of a constant density we did not obtain qualitative differences between the results of the MCT and the findings of usual cell theories. Therefore we shall not represent these data in detail here (see ref. 13). A short discussion of the results is given in section 5.

The calculation of thermodynamic properties dependent on the volume is of greater interest because of the qualitatively new treatment of density fluctuations of the liquid by means of the MCT compared to the usual cell-lattice models.

Above all we investigated the behaviour of the equation of state:

$$\frac{p}{\rho kT} = f(\rho).$$

The results of the semiclassical treatment are shown in fig. 3 and fig. 4. The quantum-statistical data are drawn in fig. 6, fig. 7, fig. 8. The numerical values of the used input parameters are presented in the figures (corresponding to the general remarks given above). The most important fact we have found by the classical treatment is a significant correlation between the shape of the cell size distribution $f_c(r)$ and the behaviour of the equation of state. Using the

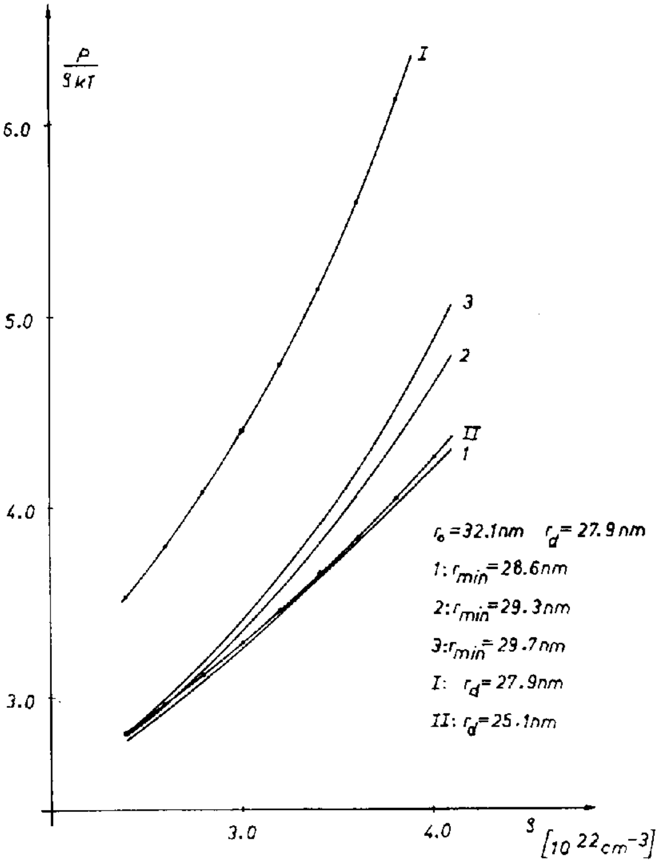

Fig. 3. Semiclassical equation of state in the MCT (curves 1, 2, 3) compared to usual cell theory results (curves I, II) for neon.

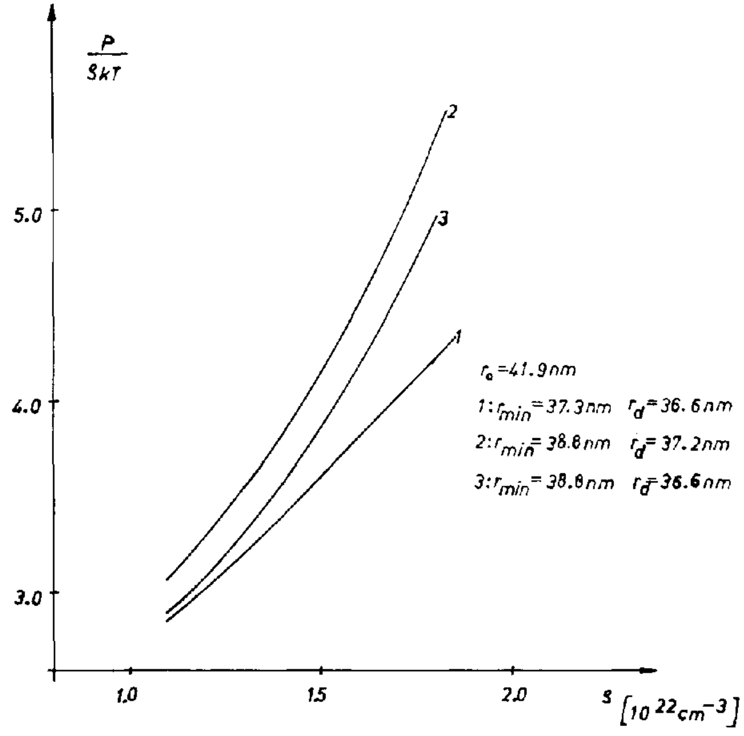

Fig. 4. Semiclassical equation of state (methane).

Γ-distribution to modelize $f_c(r)$ a variation of the parameter difference $r_0 - r_{min}$ in this function (compare fig. 2) shows a considerable change of the rise of the compressibility factor $p/\rho kT$ versus ρ. By diminuation of $r_0 - r_{min}$ we observe in the equation of state a transition from an almost linear course (curve 1 in fig. 3) to a behaviour with a more increasing rise (curve 3 in fig. 3). In case of a fixed distribution $f_c(r)$ a change of the particle diameter essentially leads to a parallel displacement of the curves without any significant variation of the shape (fig. 4). We found these characteristics not only for liquid neon (fig. 3) but also for the other investigated systems particularly for liquid methane (fig. 4) and its isotopes.

For comparison in fig. 3 (curves I and II) the results are given of a corresponding simple cell theory, i.e. a Lennard-Jones–Devonshire cell theory[1]) using the cell potential of eq. (25). In case of quantum-statistics we do not find such simple correlations between the input parameters of the MCT and the behaviour of the equation of state.

To get a review about the possible results, obtained by the variation of the model parameters, it was necessary to estimate a relatively large number of *PV*-isothermes (about 200). Most of these calculations are done for neon[13]).

In this paper we intend to summarize the most important information and the main features of these extensive data. The calculation of thermodynamic isotope effects shall be represented in a separate paper[14]).

In order to test the consistency of the results we have studied the correspondence of the quantum-theoretical data to the classical quantities in a range of higher temperatures up to about 160 K. The transition to the classical behaviour could be confirmed in all the investigated cases.

In the medium and upper temperature interval (about 60 K . . . 160 K) the behaviour is very similar to the semiclassical case showing the same characteristic dependence of the shape of the equation of state from the parameter difference $r_0 - r_{\min}$ (see above).

In general for the same density the quantum-statistical compressibility factors are greater than the semiclassical values. The differences are growing

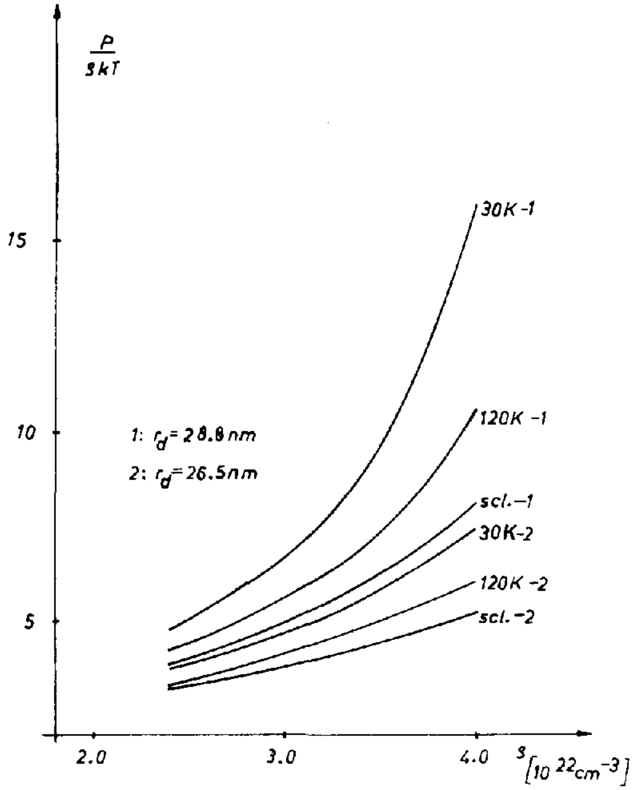

Fig. 5. Quantum-theoretical and semiclassical equation of state in the simple cell theory (neon).

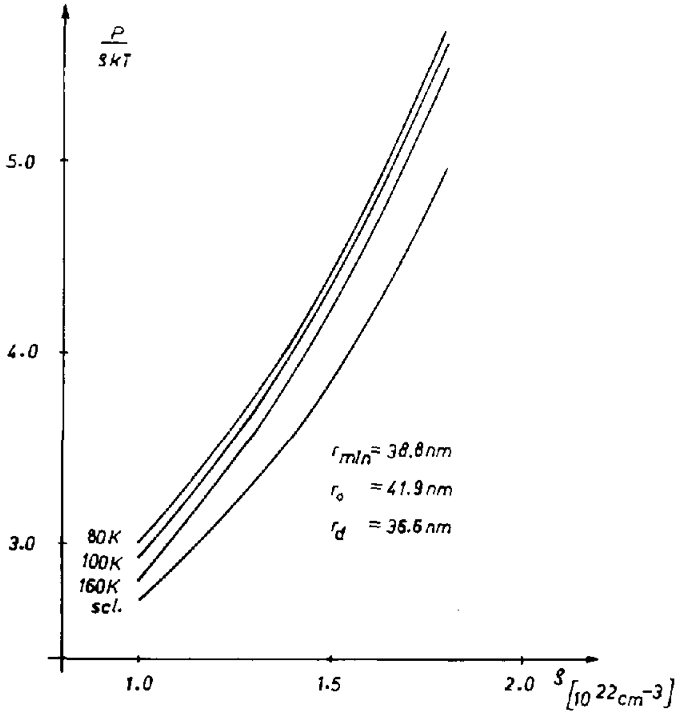

Fig. 6. Quantum-theoretical equation of state (methane).

with decreasing temperatures (neon: fig. 7; methane: fig. 6). In case of volume variations the derivations of the isothermes from the semiclassical curves increase with growing density (compare again figs. 6 and 7). This is almost the same behaviour, which is well known from conventional cell theories.

For comparison the results of an adequate simple cell theory are represented in fig. 5. There are given semiclassical and low temperature quantum-statistical calculations with particle diameters corresponding to the upper and under limitation of the variation range of r_d. It is shown that in the high density region the MCT-equation of state will not so extremely increase as it is found in the usual lattice-cell theory. In the low temperature range however the MCT-calculations lead to an equation of state depending on the model parameters in a more complicated form (30 K curves in figs. 7 and 8). Particularly the difference $r_{min} - r_d$ representing the minimal cell size in the structure, is important for a classification of the results.

If $r_{min} - r_d$ is greater than a "critical" value the behaviour of the compressibility factor is the same in the low temperature range and in the high temperature range (figs. 6 and 7). But using a reduced value of $r_{min} - r_d$ we observe some unexpected properties of the equation of state.

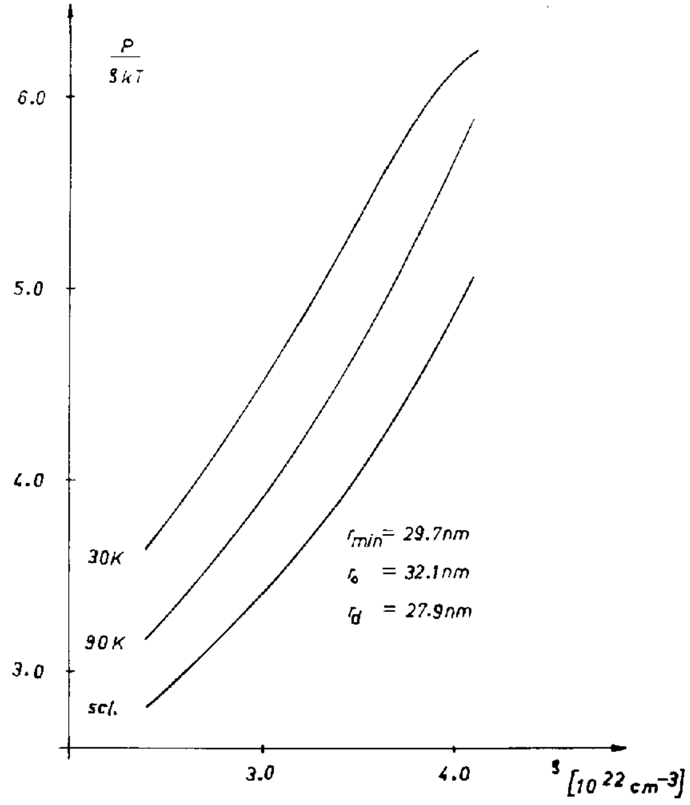

Fig. 7. Quantum-theoretical equation of state (neon).

This is shown in fig. 8 (30 K) where only for low densities the compressibility factor increases in a usual way; but with growing density a maximum of $p/\rho kT$ occurs followed by a visible decrease. This effect increases with diminuation of $r_{\min} - r_d$; it weakens with rising temperature and disappears in the correspondence transition to the semiclassical data.

For neon we found a critical value of $r_{\min} - r_d \leqslant 1.8$ nm almost independent on the selection of the other model parameters (i.e. a normal behaviour of the equation of state is observed by use of $r_{\min} - r_d > 1.8$ nm).

For methane these low temperature phenomena do not play any important role. The liquid phase of this system exists in such a temperature range (triple point temperature $T_t \approx 90.7$ K) that we observe always a normal behaviour of the equation of state (fig. 6). In a comparable temperature interval the quantum-theoretical calculations show for neon (figs. 7 and 8) and for methane (fig. 6) and for isotopes of these liquids the same qualitative features. This is quite similar as in the semiclassical case.

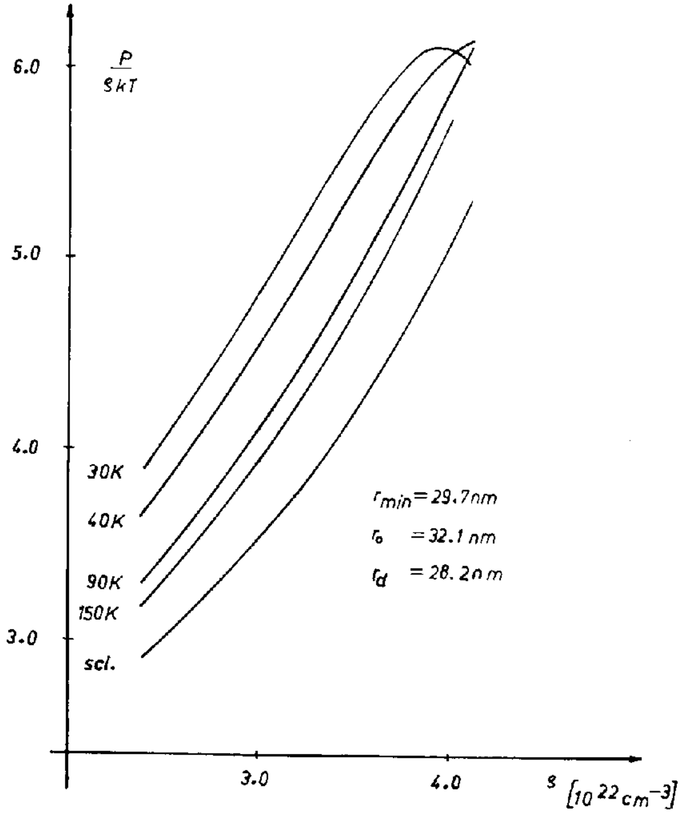

Fig. 8. Quantum-theoretical equation of state using a special set of model parameters (neon).

5. Discussion and conclusions

First we make some general remarks on the temperature dependence of thermodynamic quantities. The formal representation of the MCT (section 3) shows that some thermodynamic functions (free energy F, internal energy U, entropy S, heat capacity C_v) can written in the following manner

$$A(T, V) = \sum_i N_{r_i}(V) A_{r_i}(T). \tag{30}$$

A_{r_i} means the corresponding thermodynamic quantity (per particle) in an adequate simple cell theory using a fixed cell radius r_i. The representation eq. (30) is valid because the estimation of these thermodynamic functions does not require the derivation of the partition function with respect to the volume. It is evident to interpret the quantities represented by eq. (30) as a weighted average over the corresponding functions in a simple cell theory. The weight factor is given by the number of particles contained in cells of the radius r_i. For that reason the temperature dependence of these quantities should agree qualitatively with the behaviour found in usual cell theories. Both the semiclassical and the quantum-statistical calculations confirmed completely this expectation (see section 4).

A quite other situation is given investigating the volume dependence of thermodynamic quantities. This is due to the qualitatively new technique of the description of volume changes within the framework of the MCT. The calculations of the equation of state presented in section 4 show significant correlations between the compressibility factor $p/\rho kT$ versus ρ and the cell size distribution $f_c(r)$.

For a discussion we will compare the MCT-data with the usual lattice cell theory results. Additionally we shall give some remarks to experimental *PVT*-data and to computer simulations. Fig. 3 shows the results of the calculations of the semiclassical equation of state. Using the same particle diameter r_d the simple cell model leads to larger values of $p/\rho kT$ at the same density than the MCT does. Simultaneously the simple cell theory curves rise more compared to the MCT data (fig. 3, curve I).

A reduction of r_d in the simple cell theory (curve II) yields a decrease of $p/\rho kT$ to the order of magnitude of the MCT-results connected with a considerable weakening of the rise of $p/\rho kT$ versus ρ. This is due to the fact that the particle diameter r_d is the only adjustable parameter of the theory determining both the magnitude of the compressibility factor and the rise of the isothermes. Compared to it the MCT permits alternations of the rise of $p/\rho kT$ versus ρ almost independently of the absolute values of the compressibility factors by variation of the cell size distribution $f_c(r)$. Using for $f_c(r)$ the Γ-distribution eq. (11) this is possible by variation of $r_0 - r_{\min}$ (see section 4).

Varying the diameter r_d the magnitude of $p/\rho kT$ can be changed without a significant alteration of the shape of the isothermes. These possibilities are important for a description of experimental *PVT*-data. Although we have not done a special fit of the model parameters (see section 4) a comparison with the experimental equation of state (neon[17]) shows clearly that the MCT represents the data better than the usual cell theory does.

The MCT-values of the compressibility factor are lower, than the simple cell theory results and yield altogether a better description of the *PVT*-data, where the rise of the equation of state can be well represented (fig. 3, curve 3). This tendency is confirmed by computer simulations of the equation of state too (for instance[20]).

The quantum-theoretical calculations of the equation of state are concentrated on such sets of parameters leading in the semiclassical case to an approximate representation of the experimentally found rise of the isothermes.

In the MCT the quantum-statistical deviations from the semiclassical results behave in most of the cases similar as in the usual cell model. Some special features appear only in the high density range. Thus we do not find such an extremely (unrealistic) increase of the equation of state in this region. For special sets of parameters even a weak decrease of $p/\rho kT$ versus ρ is obtained in the vicinity of the upper density limit (compare section 4). Summarizing both the semiclassical and the quantum-theoretical calculations of the equation of state we can state that – depending on the choice of the cell size distribution – the MCT provides results which exceed essentially the possibilities of conventional cell theories and lead to an improved description of experimental *PVT*-data.

However, it is to emphasize that the presented calculations are not yet to be regarded as an optimal treatment of the thermodynamic behaviour of simple liquids on the basis of our model. The purpose of the calculations is a representation of the general features of a cell theory including a distribution of cells of different sizes compared to a simple lattice-cell model with a uniform size of the cells. To get a satisfactory description of experimental *PVT*-data it may be necessary to use an optimal set of model parameters as well as a more realistic cell potential including attractive forces between the molecules (for instance a Lennard-Jones–Devonshire potential[1])). It is encouraging that even the presented simple version of the theory permits a better representation of experimental results. There are interesting connections between the structural assumptions of the MCT and Bernal's model of randomly close packed structures of hard spheres too[15,16]).

Interpreting a randomly distributed system of particles in terms of a cell model we follow some suggestions of Finney[16]) dividing the liquid volume into a set of Voronoi polyhedra where every polyhedron is associated with exactly one particle. Thus each Voronoi polyhedron can be regarded as a cell containing one particle. Finney gives distributions of cell volumina obtained by the randomly close packed system. These look to be consistent with the distribution of cell sizes used in our model.

So we have a further strong support for the necessity to introduce different cell sizes in a satisfactory cell model of the liquid structure (see also Hoover et al.[8])). Simultaneously the study of random arrangements of particles can provide informations about the cell size distribution $f_c(r)$ which do not depend on experimental structural data.

An extension of the MCT to more complicated liquids should be possible by the introduction of distributions of non spherical (simple symmetrical) cells and by the use of more complex cell potentials. In general the MCT should be of interest not only for the calculation of thermodynamic properties of real liquids; also the presented generalization of a cell structure without any lattice should be suitable for a study of the possibilities and the limitations of the cell picture in the theory of liquids.

Taking into account the flexibility of structural description by use of suitable cell size distributions and the possibilities to generalize the model the MCT may be regarded as a hopeful starting point not only for a treatment of structural and thermodynamic properties of simple liquids but also for an investigation of more complicated systems including liquids consisting of nonspherical particles.

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