

THERMODYNAMIC PROPERTIES OF SIMPLE FLUIDS IN THE HARD SPHERE REFERENCE SYSTEM*

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The zeroth-order approximation of the repulsive configurational internal energy $U_r^0(T, \rho)$ for different temperatures and densities are obtained by scaling the curve of the repulsive configurational internal energy $U_r^{\text{hs}}(\rho)$ calculated in the hard sphere reference system with diameter σ independent of temperature and density. Similarly the zeroth-order approximation of the attractive configurational internal energy $U_a^0(T, \rho)$ for different temperatures and densities are obtained by scaling the curve of the attractive configurational internal energy $U_a^{\text{hs}}(\rho)$ calculated in the hard sphere reference system also with diameter σ . The sum $U^0 = U_r^0 + U_a^0$ which is the total configurational internal energy, the virial, the residual free energy and the residual entropy are also calculated. The obtained results are compared with "experimental" data and with the calculations of Verlet and Weis. Some very simple criteria of choosing the diameter $d(T)$ of a hard sphere for the reference system are also discussed.

1. Introduction

In recent years a number of statistical-mechanical perturbation theories [1-5] have been developed to give thermodynamic properties in excellent agreement with computer simulations at densities and temperatures characteristic of both gases and liquids. The structure of simple liquids is determined mostly by the repulsive part of the potential. Thus in the perturbation theory we expand the logarithm of the configurational partition function Q_N for the system in a Taylor series about the value $\ln Q_N^{\text{ref}}$ for some reference system whose molecules interact according to the repulsive part of the potential. With this result one can write the Taylor series expression for the Helmholtz free energy. The configurational internal energy and other properties are calculated by thermodynamic relations.

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Malesiński [6] has suggested that the configurational internal energy U for the Lennard-Jones fluid may be divided into the repulsive configurational internal energy U_r and the attractive configurational internal energy U_a defined by

$$U_r = \left\langle \sum_{i < j} \varphi_r(r_{ij}) \right\rangle = 2\pi N \rho \int_0^{\infty} \varphi_r(r) g(r; T, \rho) r^2 dr, \quad (1)$$

$$U_a = \left\langle \sum_{i < j} \varphi_a(r_{ij}) \right\rangle = 2\pi N \rho \int_0^{\infty} \varphi_a(r) g(r; T, \rho) r^2 dr, \quad (2)$$

where

$$\varphi_r(r) = c(m, n) \varepsilon \left(\frac{\sigma}{r} \right)^m, \quad (3)$$

$$m > n$$

$$\varphi_a(r) = -c(m, n) \varepsilon \left(\frac{\sigma}{r} \right)^n, \quad (4)$$

and $\langle \dots \rangle$ denotes the average value.

The isotherms of U_r and U_a are monotonic functions of density. The isotherms of $U = U_r + U_a$ and other thermodynamic properties which are related to U_r and U_a , are not necessarily monotonic functions of density. The monotonic properties of U_r and U_a make possible the observation of the creation of minima on curves U and other thermodynamic properties.

In previous papers we have investigated U_r , U_a and U in the hard sphere reference system with diameter σ independent of temperature and density [7-9] and in the soft sphere reference system [10]. In the first reference system poor results are obtained. The second reference system reproduces U_r and U_a quite well at high temperatures. Now we present the calculations of U_r and U_a for the Lennard-Jones (12-6) potential in the hard sphere reference system with diameter $d(T)$. Other thermodynamic properties (virial, residual free energy, residual entropy) related to U_r and U_a are also presented.

2. Scaling properties of the configurational internal energy in the hard sphere reference system with diameter $d(T)$

From Eq. (1) and (2) one can see that to calculate U_r and U_a we should know the radial distribution function $g(r; T, \rho)$. Because we do not know $g(r; T, \rho)$, we use different approximate forms of this function. One of the possible approximations is the assumption

$$g(r; T, \rho) \approx g_0(r; T, \rho), \quad (5)$$

where $g_0(r; T, \rho)$ is the radial distribution function of hard spheres with diameter $d(T)$.

Now we consider the approximation of U_r and U_a defined by

$$U_r^0(T, \varrho) = 2\pi N \varepsilon \varrho c \int_0^\infty \left(\frac{\sigma}{r}\right)^m g_0(r; T, \varrho) r^2 dr, \quad (6)$$

$$U_a^0(T, \varrho) = -2\pi N \varepsilon \varrho c \int_0^\infty \left(\frac{\sigma}{r}\right)^n g_0(r; T, \varrho) r^2 dr. \quad (7)$$

In previous papers [7, 8] we have discussed U_r^{hs} and U_a^{hs} defined by

$$U_r^{\text{hs}}(\varrho\sigma^3) = 2\pi N \varepsilon \varrho \sigma^3 c \int_0^\infty \left(\frac{\sigma}{r}\right)^m g_{\text{hs}}\left(\frac{r}{\sigma}; \varrho\sigma^3\right) \left(\frac{r}{\sigma}\right)^2 d\left(\frac{r}{\sigma}\right), \quad (8)$$

$$U_a^{\text{hs}}(\varrho\sigma^3) = -2\pi N \varepsilon \varrho \sigma^3 c \int_0^\infty \left(\frac{\sigma}{r}\right)^n g_{\text{hs}}\left(\frac{r}{\sigma}; \varrho\sigma^3\right) \left(\frac{r}{\sigma}\right)^2 d\left(\frac{r}{\sigma}\right), \quad (9)$$

with $g_{\text{hs}}(r/\sigma; \varrho\sigma^3)$ adopted from the Percus-Yevick approximation [11, 12]. Barker and Henderson [13] have calculated by the Monte Carlo method the $g_{\text{hs}}(r/\sigma; \varrho\sigma^3)$ for $1 < r/\sigma < 2.3$. So we calculated $U_r^{\text{hs}}(\varrho)$ and $U_a^{\text{hs}}(\varrho)$ for density 0.2–0.9 with $g_{\text{hs}}(r/\sigma; \varrho\sigma^3)$ from Monte Carlo data for above the range of r/σ (the computed values of $g_{\text{hs}}(r/\sigma; \varrho\sigma^3)$ was multiplied by 108/107) and with $g_{\text{hs}}(r/\sigma; \varrho\sigma^3)$ from the Percus-Yevick approximation for larger r/σ . For $r/\sigma > 4$ or $r/\sigma > 6$ we put $g_{\text{hs}}(r/\sigma; \varrho\sigma^3) = 1$. Thus the calculated values of the $U_r^{\text{hs}}(\varrho)$ and $U_a^{\text{hs}}(\varrho)$ are presented in the following Table.

TABLE I

The values of U_r^{hs} and U_a^{hs} calculated for the Lennard-Jones (12-6) potential in the hard sphere reference system of diameter σ

$\varrho\sigma^3$	U_r^{hs}	U_a^{hs}
0.1	0.3104	-0.8957
0.2	0.6940	-1.9241
0.3	1.1577	-3.0780
0.4	1.7340	-4.3852
0.5	2.4328	-5.8454
0.6	3.2868	-7.4755
0.7	4.3135	-9.2688
0.8	5.5770	-11.2657
0.9	7.1090	-13.4576

Now we show that $U_r^0(T, \varrho)$ and $U_a^0(T, \varrho)$ may be appropriately expressed by $U_r^{\text{hs}}(\varrho)$ and $U_a^{\text{hs}}(\varrho)$ i.e. the curves $U_r^0(T, \varrho)$ may be obtained by scaling the curve $U_r^{\text{hs}}(\varrho)$ and the curves $U_a^0(T, \varrho)$ may be obtained by scaling the curve $U_a^{\text{hs}}(\varrho)$.

After introducing the reduced distance $x = r/d$ from Eq. (6) we obtain

$$\begin{aligned}
 U_r^0(T, \varrho) &= 2\pi N\varepsilon\varrho d^3 c \int_1^{\infty} \left(\frac{\sigma}{xd}\right)^m g_0(x; \varrho d^3) x^2 dx \\
 &= 2\pi N\varepsilon\varrho d^3 c \left(\frac{d}{\sigma}\right)^{-m} \int_1^{\infty} x^{-m} g_0(x; \varrho d^3) x^2 dx \\
 &= d^{*-m} \cdot 2\pi N\varepsilon\varrho d^3 c \int_1^{\infty} x^{-m} g_0(x; \varrho d^3) x^2 dx,
 \end{aligned} \tag{10}$$

where $d^* = d/\sigma$ and $T^* = kT/\varepsilon$.

For $\varrho_1 d^3 = \varrho_2 \sigma^3$ there is equality

$$2\pi N\varepsilon\varrho_1 d^3 c \int_1^{\infty} x^{-m} g_0(x; \varrho_1 d^3) x^2 dx = 2\pi N\varepsilon\varrho_2 \sigma^3 c \int_1^{\infty} x^{-m} g_{hs}(x; \varrho_2 \sigma^3) x^2 dx = U_r^{hs}(\varrho_2 \sigma^3). \tag{11}$$

Thus

$$U_r^0(T^*, \varrho_1 d^3) = d^{*-m} U_r^{hs}(\varrho_2 \sigma^3) \quad \text{for } \varrho_1 d^3 = \varrho_2 \sigma^3. \tag{12}$$

In a similar way we obtain

$$U_a^0(T^*, \varrho_1 d^3) = d^{*-n} U_a^{hs}(\varrho_2 \sigma^3) \quad \text{for } \varrho_1 d^3 = \varrho_2 \sigma^3. \tag{13}$$

3. The configurational internal energy in the hard sphere reference system with diameter $d(T)$ chosen in a simple way

Division of intermolecular potential into an unperturbed part $\varphi_0(r)$ defined by

$$\varphi_0(r) = \begin{cases} \varphi(r) + \varepsilon & \text{for } r < r_{\min} \\ 0 & \text{for } r \geq r_{\min} \end{cases} \tag{14}$$

and a perturbing part $\varphi_1(r)$ defined by

$$\varphi_1(r) = \begin{cases} -\varepsilon & \text{for } r < r_{\min} \\ \varphi(r) & \text{for } r \geq r_{\min} \end{cases} \tag{15}$$

seems more appropriate than any other division. From this division one would expect that at low temperatures the nearest distance between molecules would be a little smaller than r_{\min} and larger than σ . With an increase in temperature the distance of closest approach would become smaller and for a sufficiently high temperature may be smaller than σ .

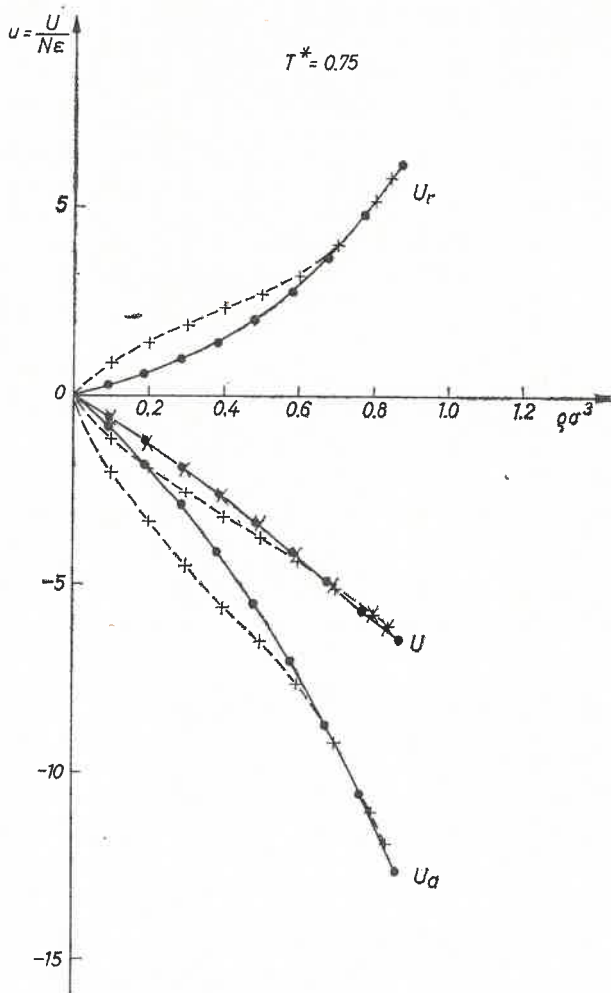


Fig. 1. The isotherms $T^* = 0.75$ of the repulsive configurational internal energy U_r , of the attractive configurational internal energy U_a , of the total configurational internal energy U for the Lennard-Jones (12-6) potential; ●●● calculated data in the hard sphere reference system of diameter $d(T)$ determined by Eq. (18); ××× the Verlet and Weis results; +++ "experimental" data

The Barker and Henderson choice of $d(T)$ is obtained from the division of the intermolecular potential at the point $r = \sigma$ for which $\varphi(\sigma) = 0$ and the diameter $d(T)$ is always smaller than σ . Analysing our results for U_r^0 and U_a^0 one can see that the diameter $d(T, \rho)$ defined by Verlet and Weis rises with temperature too slowly. It seems that a better value of diameter d would be between $d(T)$ defined by Barker and Henderson and $d(T, \rho)$ defined by Verlet and Weis.

From the Maxwell distribution of velocities we may see that some particles have smaller nearest distances than others. One may raise a question, which nearest distance represents the N particle system interacting by a $\varphi(r)$ potential in the best way. Andrews [14]

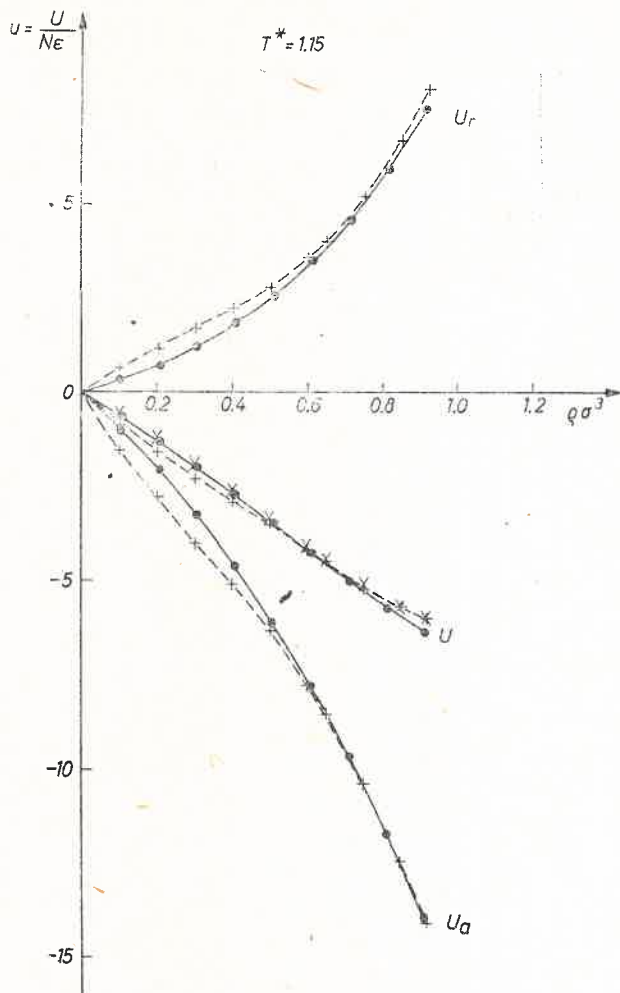


Fig. 2. The isotherms $T^* = 1.15$ of the repulsive configurational internal energy U_r , of the attractive configurational internal energy U_a , of the total configurational internal energy U for the Lennard-Jones (12-6) potential; ●●● calculated data in the hard sphere reference system of diameter $d(T)$ determined by Eq. (18); ××× the Verlet and Weis results; +++ "experimental" data

determined the diameter $d(T)$ by the equation

$$\varphi(d) = \frac{3}{2}kT \quad (16)$$

and obtained good agreement with "experimental" data.

Eq. (12) and (13) give us a simple method of examining the criteria of choosing the diameter d . Our calculations of U_r^0 , U_a^0 and $U^0 = U_r^0 + U_a^0$ indicate that the diameter $d(T)$ determined by Eq. (16) is too small. One may obtain better results if $d(T)$ is determined by equation

$$\varphi_0(d) = \frac{3}{2}kT. \quad (17)$$

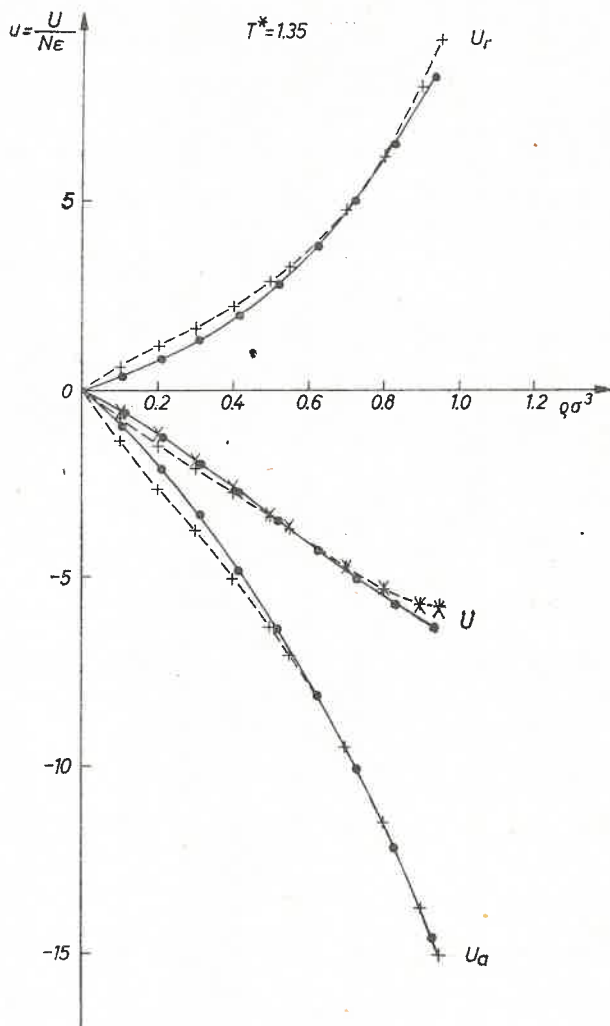


Fig. 3. The isotherms $T^* = 1.35$ of the repulsive configurational internal energy U_r , of the attractive configurational internal energy U_a , of the total configurational internal energy U for the Lennard-Jones (12-6) potential; ●●● calculated data in the hard sphere reference system of diameter $d(T)$ determined by Eq. (18); ××× the Verlet and Weis results; +++ "experimental" data

The best agreement between our U_r^0 , U_a^0 , U^0 and "experimental" U_r , U_a , U is obtained if we determine the $d(T)$ by the criterion

$$\varphi_0(d) = kT. \quad (18)$$

The results of our calculations of U_r^0 , U_a^0 and U^0 from Eq. (12) and (13) with $d(T)$ determined by Eq. (18) are presented in Fig. 1—4. At $T^* = 0.75$ our results for U^0 and Verlet and Weis results for U are almost on the same curve. Our results for U^0 and the Verlet and Weis [15] results for U coincide up to a rather high density which slowly decreases

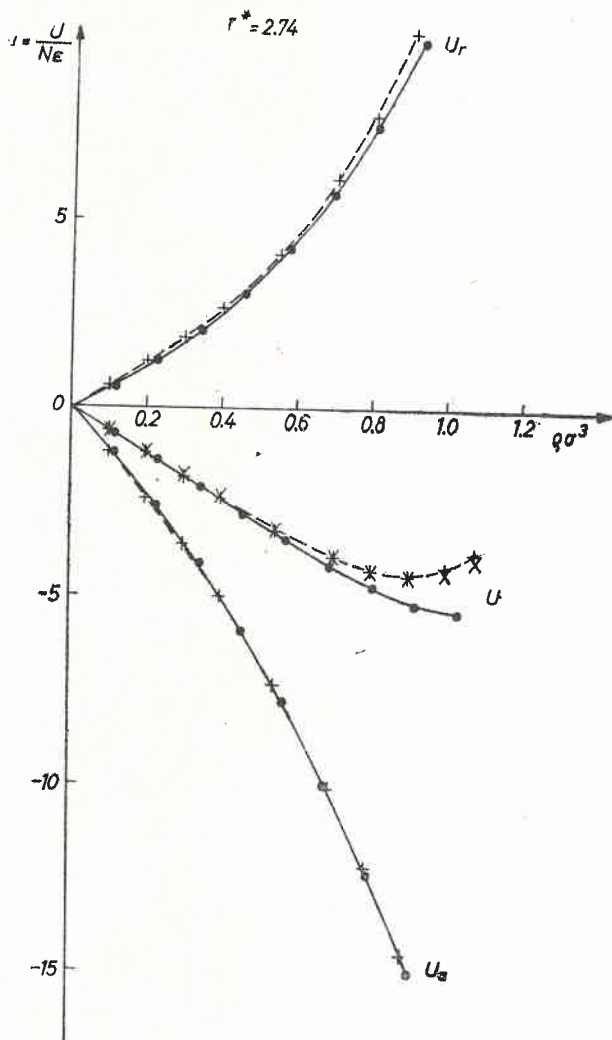


Fig. 4. The isotherms $T^* = 2.74$ of the repulsive configurational internal energy U_r , of the attractive configurational internal energy U_a , of the total configurational internal energy U for the Lennard-Jones (12-6) potential; $\bullet\bullet\bullet$ calculated data in the hard sphere reference system of diameter $d(T)$ determined by Eq. (18); $\times\times\times$ the Verlet and Weis results; $+++$ "experimental" data

with an increase in temperature. For the larger densities the results of Verlet and Weis are in better agreement with "experimental" data.

Now we will try to discuss the fact that the "experimental" data are well reproduced by choosing $d(T)$ from Eq. (18). From the Maxwell distribution of velocities we know that the largest number of particles have velocity V about $(2kT/m)^{1/2}$, the velocity at which the distribution has the maximum. This velocity then corresponds to the classical distance of closest approach for particles with relative kinetic energy equal to kT .

4. The virial, the residual free energy and the residual entropy

The virial is defined by

$$\mathcal{W}(\vec{r}^N) = -\frac{1}{3} \sum_i \vec{r}_i \cdot \frac{\partial}{\partial \vec{r}_i} \Phi(\vec{r}^N). \quad (19)$$

For the Lennard-Jones potential it may be divided (as the configurational internal energy was) into a repulsive virial and an attractive virial i.e.

$$\mathcal{W}(\vec{r}^N) = \mathcal{W}_r(\vec{r}^N) + \mathcal{W}_a(\vec{r}^N), \quad (20)$$

where

$$\mathcal{W}_r(\vec{r}^N) = \frac{m}{3} \sum_{i < j} \varphi_r(r_{ij}), \quad (21)$$

$$\mathcal{W}_a(\vec{r}^N) = \frac{n}{3} \sum_{i < j} \varphi_a(r_{ij}). \quad (22)$$

Thus the average values of the virial is

$$\langle \mathcal{W}(\vec{r}^N) \rangle \equiv W = \frac{m}{3} U_r + \frac{n}{3} U_a. \quad (23)$$

Substituting Eq. (12) and (13) into Eq. (23) we obtain

$$w = \frac{W}{N\varepsilon} = \frac{2}{3} \pi c \rho d^3 [m d^{* - m} \int_1^\infty x^{-m} g_{hs}(x; \rho d^3) x^2 dx - n d^{* - n} \int_1^\infty x^{-n} g_{hs}(x; \rho d^3) x^2 dx]. \quad (24)$$

The results of our calculations of W for the Lennard-Jones (12—6) potential from Eq. (24) with $d(T)$ determined by Eq. (18) are presented in Fig. 5. In this figure we have also plotted "experimental" curves. One can see that our curves have the right depth of minima and are in good agreement with "experimental" curves. Only for large densities do our results appreciably deviate from "experimental" data. Comparing the curves of the configurational internal energy and the virial we see that the large discrepancies at low temperatures for U_r and U_a become smaller for U and W because there is some cancelation in the deviations of U_r and U_a . For curves of W the cancelation is greater than for curves of U .

The residual free energy is defined by

$$\begin{aligned} F_{res} &= - \int_{\infty}^V (p - p_{id}) dV = N \int_0^{\rho} \left(\frac{p}{\rho} - \frac{p_{id}}{\rho} \right) \frac{d\rho}{\rho} \\ &= \int_0^{\rho} W \frac{d\rho}{\rho} = \int_0^{\rho} \left(\frac{m}{3} U_r + \frac{n}{3} U_a \right) \frac{d\rho}{\rho}. \end{aligned} \quad (25)$$

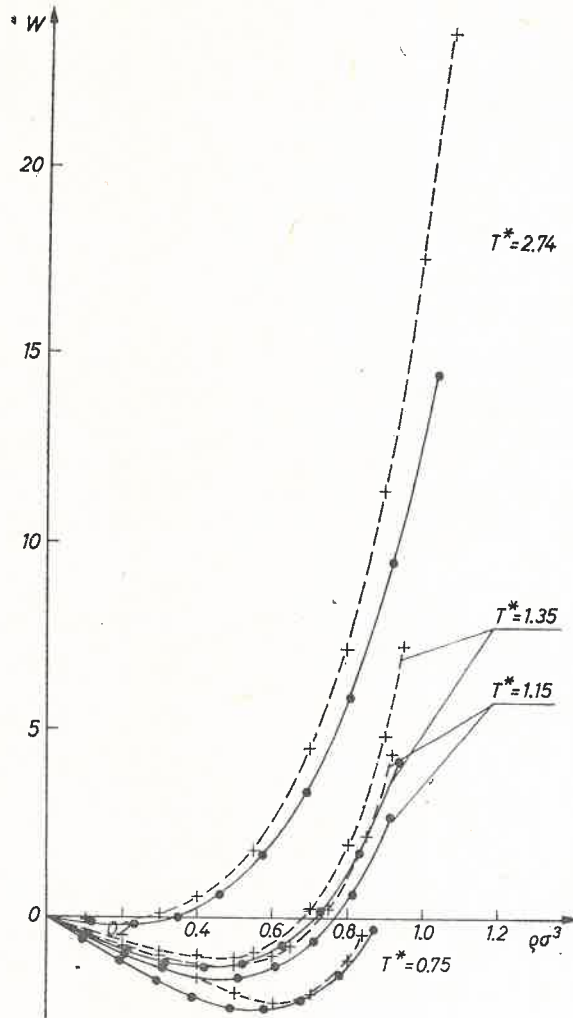


Fig. 5. The isotherms of the virial for the Lennard-Jones (12-6) potential; ——— calculated data; - - - "experimental" data

From Eq. (12) and (13) we have

$$\begin{aligned}
 f_{\text{res}}(T^*, \varrho_1 d^3) &= \frac{F_{\text{res}}}{N_E} = \frac{2}{3} \pi c m \int_0^{\varrho_1 d^3} d(\varrho_1 d^3) \int_1^{\infty} (x d^*)^{-m} g_{\text{hs}}(x; \varrho_1 d^3) x^2 dx \\
 &\quad - \frac{2}{3} \pi c n \int_0^{\varrho_1 d^3} d(\varrho_1 d^3) \int_1^{\infty} (x d^*)^{-n} g_{\text{hs}}(x; \varrho_1 d^3) x^2 dx \\
 &= \frac{2}{3} \pi c m d^{*-m} \int_0^{\varrho_2 \sigma^3} d(\varrho_2 \sigma^3) \int_1^{\infty} x^{-m} g_{\text{hs}}(x; \varrho_2 \sigma^3) x^2 dx \\
 &\quad - \frac{2}{3} \pi c n d^{*-n} \int_0^{\varrho_2 \sigma^3} d(\varrho_2 \sigma^3) \int_1^{\infty} x^{-n} g_{\text{hs}}(x; \varrho_2 \sigma^3) x^2 dx, \quad (26)
 \end{aligned}$$

with $\rho_1 d^3 = \rho_2 \sigma^3$. For $\rho d^3 \rightarrow 0$, $U_r \rightarrow 0$ and $U_a \rightarrow 0$ because the integrals are multiplied by density. The integrals in U_r and U_a , contained also in f_{res} go to values dependent on temperature. For $\rho d^3 \rightarrow 0$ and for $x \geq 1$ the function $g_{hs}(x; \rho d^3) \rightarrow 1$ and for $x < 1$

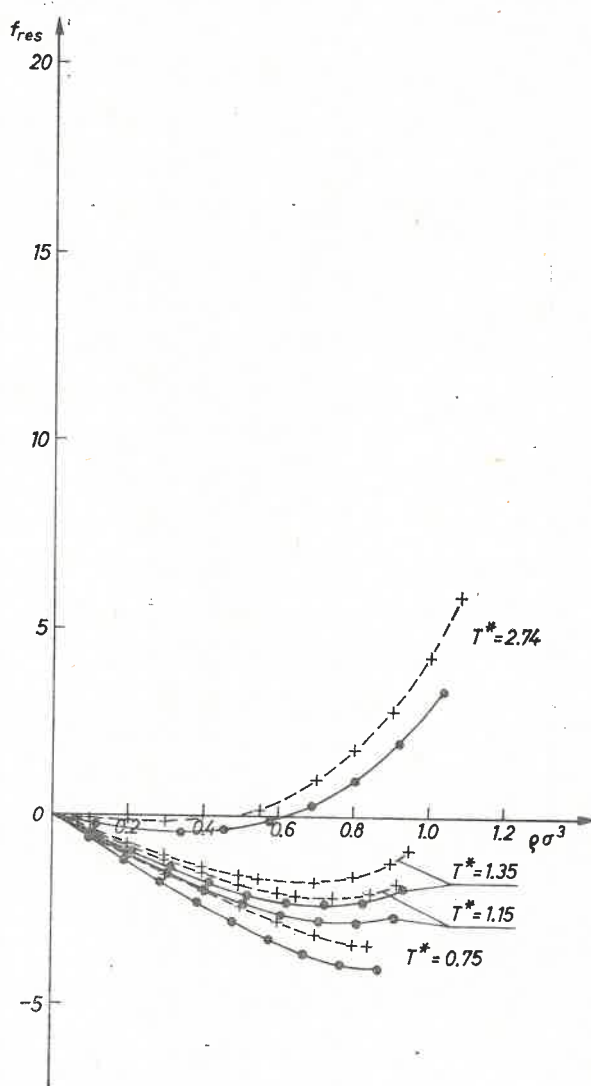


Fig. 6. The isotherms of the residual free energy for the Lennard-Jones (12-6) potential; ——— calculated data; - - - "experimental" data

is zero but do not go to $e^{-\beta\phi}$ as in real systems. In Fig. 6 we plotted the isotherms of f_{res} for the Lennard-Jones (12-6) potential calculated by Eq. (25) choosing $d(T)$ by Eq. (18). The isotherms of f_{res} are lower than the appropriate "experimental" isotherms but are in good agreement with them.

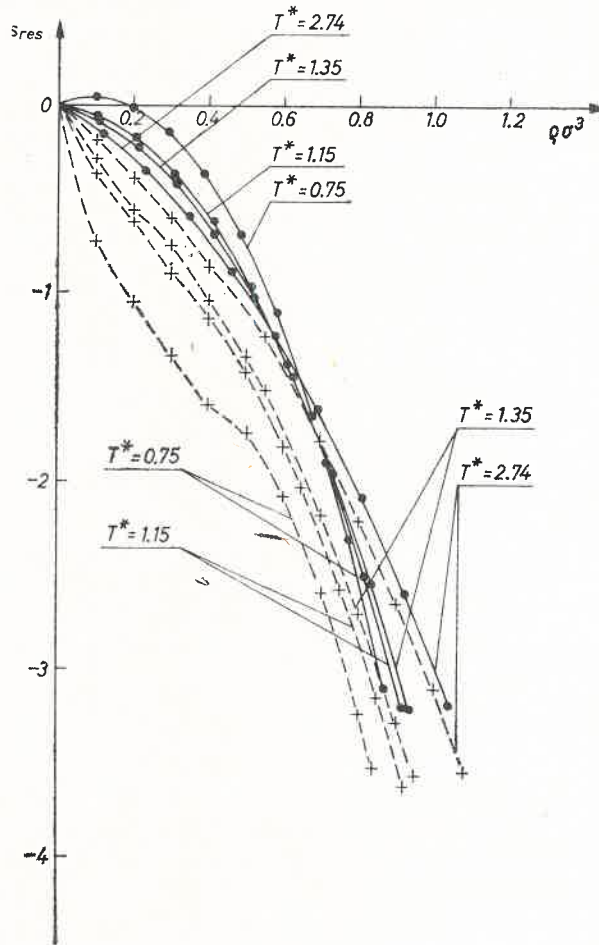


Fig. 7. The isotherms of the residual entropy for the Lennard-Jones (12-6) potential; ——— calculated data; - - - "experimental" data

The residual entropy may be calculated by

$$TS_{\text{res}} = U - F_{\text{res}}. \quad (27)$$

Thus one may obtain

$$s_{\text{res}}(T^*, \rho d^3) = \frac{S_{\text{res}}}{Nk} = \frac{2\pi c}{T^*} \left\{ \rho d^3 \int_1^{\infty} [(xd^*)^{-m} - (xd^*)^{-n}] g_{\text{hs}}(x; \rho d^3) x^2 dx \right. \\ \left. - \int_0^{\rho d^3} d(\rho d^3) \int_1^{\infty} \left[\frac{m}{3} (xd^*)^{-m} - \frac{n}{3} (xd^*)^{-n} \right] g_{\text{hs}}(x; \rho d^3) x^2 dx \right\}. \quad (28)$$

The isotherms of s_{res} calculated by Eq. (28) for the Lennard-Jones (12—6) potential with $d(T)$ determined by Eq. (18) are plotted in Fig. 7. The isotherms of s_{res} are always above the appropriate "experimental" isotherms. At low temperatures and low densities $(\partial s_{\text{res}}/\partial \rho)_T > 0$, it is not in agreement with "experimental" data. At intermediate and large densities we obtain the right sign of $(\partial s_{\text{res}}/\partial \rho)_T$. The calculated curves cross themselves, whereas the "experimental" curves do not cross themselves. At large densities calculated curves of s_{res} are closer to the "experimental" curves than at low densities.

5. Discussion

In doctoral dissertation was discussed U_r , U_a and other thermodynamic properties calculated on the base of Eq. (12) and (13) choosing the parameter $d(T)$ by

$$d(T) = \int_0^{\sigma} \{1 - \exp[-\beta\varphi(r)]\} dr, \quad (29)$$

where $\varphi(\sigma) = 0$, and choosing the parameter $d(T, \rho)$ by

$$d(T, \rho) = d_{\beta}(T) \left[1 + \frac{\sigma_1(\rho)}{2\sigma_0(\rho)} \cdot \delta(T) \right], \quad (30)$$

where

$$d_{\beta}(T) = \int_0^{\infty} (1 - e^{-\beta\varphi_0}) dr, \quad (31)$$

$$\delta(T) = \frac{d}{d_{\beta}} \int_0^{\infty} \left(\frac{r}{d} - 1 \right)^2 \frac{d}{dr} e^{-\beta\varphi_0(r)} dr \approx \int_0^{\infty} \left(\frac{d}{d_{\beta}} - 1 \right)^2 \frac{d}{dr} e^{-\beta\varphi_0(r)} dr. \quad (32)$$

σ_0 and σ_1 are expressed by $y_{\text{hs}}(1, \rho)$ and its derivative. In the Percus-Yevick approximation we have

$$\frac{\sigma_1}{2\sigma_0} = \frac{1 - \frac{1}{4}\eta(1+\eta)}{(1 + \frac{1}{2}\eta)(1-\eta)}, \quad (33)$$

where $\eta = \frac{\pi}{6} \rho d^3$. We applied this relation to determine the diameter $d(T, \rho)$.

In the first case i.e. for $d(T)$ chosen by Eq. (29) we observe that the deviations of our curves U_r^0 and U_a^0 from appropriate "experimental" curves become smaller up to $T^* = 2.74$ and become larger above this temperature. The curves $U^0 = U_r^0 + U_a^0$ at low temperatures go above the curves of "experimental" U and with an increase in temperature the deviations become smaller. At $T^* = 2.74$ and $T^* = 5$ at low densities they are almost the same as the "experimental" one, but at large densities they go below the "experimental" curve and deviations are large. The curves of W at low temperature have less deep and shifted to lower densities minima than the appropriate "experimental" one. The curves of f_{res} at low temperatures go above the appropriate "experimental" curves.

In the second case i.e. for $d(T, \rho)$ chosen by Eq. (30) we observe that deviations of the curves U_r^0 and U_a^0 from appropriate "experimental" curves are larger than in the first case. In this approximation the values of U_r^0 are always smaller than the appropriate "experimental" values of U_r and values of U_a^0 are always higher than the appropriate "experimental" values of U_a . The curves of U^0 cross the "experimental" curves of U . The curves of W have deeper minima than the "experimental" one. The curves of f_{res} always go below the appropriate "experimental" curves.

In our calculations of thermodynamic properties below $T^* = 1.35$ there are unstable and metastable states of the system. At $T^* = 1.15$ and $\rho\sigma^3$ from 0.1 until 0.6 the system is in one of these states and at $T^* = 0.75$ in the whole presented range of densities the system is in one of these states also.

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