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# SCALED PARTICLES' MODELS AND THERMODYNAMIC PROPERTIES OF *N*-ALKANES

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The possibility of the usage of the scaled particles' models for the description of elastic and thermal properties of $n$-alkanes is analyzed. It is shown that the scaled particles' models describe the dependence of coefficient of compression and elastic module on the $n$-alkanes' density qualitatively correctly, at the same time quantitative divergence increases as density increases. The dependence of the elastic and thermal properties of $n$-alkanes on thermodynamic parameters is determined by the whole potential curve particularities (not only by its repulsive part for elastic properties or only by its attractive part for thermal properties).

## Introduction

Existence of the connection between the physical properties of liquids and their molecular structure follows from the statistical theory of the liquids. However the problem of determination of this connection is solved for limited number of cases (for simple, isotropic or slightly anisotropic liquids) because of the impossibility of the correct description of intermolecular interaction and the mathematical difficulties while solving integral equations which can not be completely removed by using numerical methods. For majority of practically important molecular liquids the statistical theory is not developed. Therefore, we have to find the connection between physical properties of liquids and their molecular structure experimentally.

Finding the equation of state which allows to describe the dependence of the equilibrium properties of the complex molecular liquids consisting of nonspherical particles not only on the thermodynamic parameters but also on their microcharacteristics is a part of the mentioned above problem.

## Experiment

The group of $n$-alkanes, from $n$-hexane to $n$-pentadecane, was taken as object of investigations. For the discussion we also used data on $CO_2$ [1] and $Ar$ [2]. The PVT data were obtained by the metal bellows method. The apparatus and the experimental procedure were described in [3]. The specific volumes were measured in the temperature range from 313 to 413 K and in the pressure range from 0.1 to 245.25 MPa. In addition to PVT data we have studied the ultrasonic velocity in the same temperature and pressure ranges by the direct pulse-echo method of the fixed distance with frequency 5 MHz [4]. Previously we had checked that there was no dispersion of ultrasonic velocity in the frequency range 1.25–10 MHz within the indicated limits of the thermodynamic parameters' change. The errors of measurement of specific volume and ultrasonic velocity were 0.2% and 0.3%, respectively. To determine the parameters of scaled particles we used $X$-ray investigation data about the C-C and C-H bond length and bond angles [5].

## Calculations and discussion

Using the obtained experimental data, we calculated the coefficient of compression $PV/RT$, elastic module $K_T$, coefficient of the thermal dilatation $\alpha_P$. The same thermodynamic properties were calculated by the scaled particles' models as well. For this aim we used the following equations [6-12]:

*Nezbeda* equation

$$PV/RT = (1 + (3\alpha - 2)\eta + (\alpha^2 + \alpha + 1)\eta^2 - \alpha(5\alpha - 4)\eta^3)/(1 - \eta)^3, \quad (1)$$

*hard sphere* equation

$$PV/RT = (1 + \eta + \eta^2 - \eta^3)/(1 - \eta)^3, \quad (2)$$

*hard sphere with attraction* equation

$$PV/RT = (1 + \eta + \eta^2 - \eta^3)/(1 - \eta)^3 - A\eta\varepsilon/k_{\mathrm{B}}T, \quad (3)$$

*soft sphere* equation

$$PV/RT = (1 + \eta\chi + \eta^2\chi^2 - \eta^3\chi^3)/(1 - \eta\chi)^3, \quad (4)$$

*soft sphere with attraction* equation

$$PV/RT = (1 + \eta\chi + \eta^2\chi^2 - \eta^3\chi^3)/(1 - \eta\chi)^3 - A\eta\chi\varepsilon/k_{\mathrm{B}}T, \quad (5)$$

*hard sphere cylinder* equation

$$PV/RT = (1+B+C+D+(B+C)^2+(1/3)D(B+1.5)C)/(1-B-C)^3, \quad (6)$$

where $\eta = (N/6V)\pi\sigma^3$, $\sigma$ is the mean collision diameter, $B = (N/4V)l\pi\sigma^2$, $l$ is the length of a particle, $C = \eta$, $\alpha = (\gamma + 1)/(3\gamma - 1)$, $\gamma = l/\sigma$, $D = (N/4V)l^2\pi\sigma$, $\chi = (293/T)^{3/n}$, $n$ is the numeral density.

Barker and Henderson have shown [13] that the consideration of the particles' attraction in the shape of rectangular well leads to the appearance of the additional term $A\eta\varepsilon/k_BT$ in the equation of state of scaled particles where $A$ is constant with the value dependent on the width of the rectangular well $Q$: $A = 4[Q^3 - 1]$,

Lebowits and Rowlinson have shown [14] that consideration of the power character of the repulsive potential dependence on the distance between particles preserves the form of the state equation, but the diameter of particles turns out to be decreasing function of temperature

$$d\eta/dT = -3\eta/k_{\mathrm{B}}T.$$

Therefore for soft spherecylinder we supposed that

$$l = l_0 \left(\frac{293}{T}\right)^{1/n}, \tag{7}$$

$l_0$ is the length of the molecule at $T = 273$ K.

Because the statistical theory is well developed only for the simple liquids it is interesting to study $Ar$ — the liquid with spherical shape of molecules, and $CO_2$ — one of the simplest liquids with nonspherical shape of molecules. We obtained the coefficient of the thermal dilatation and $PV/RT$ of Ar in a wide range of temperatures (from $T_{critical}$ to $T_{triple}$ point) and pressures (from $0.2P_{critical}$ to $2P_{critical}$) for soft particles with and without consideration of the attractive force (in a form of rectangular potential well). The best correlation with experimental data is given by the model of the soft spheres with attraction. If we use the hard attractive model, $\alpha_P$ is higher than the experimental value and $PV/RT$ is lower.

For liquid $CO_2$ we used the following $X$-ray data to calculate the parameters of models [11] : $R_{C-O}$=0.113 nm, $R_C = 0.180$ nm, $R_O = 0.136$ nm, $\gamma = 1.576$. The values of $PV/RT$ calculated by equations (1), (2), (6) and determined experimentally for $CO_2$in the undercritical and overcritical regions of thermodynamic parameters changie are given in table 1.

Table 1. Comparison of the values of $PV/RT$ for $CO_2$ calculated by equations (1), (2), and (6) with experimental data.

| $T, K$ | $PV/RT$ exper. | $PV/RT$ eq. (1) | $PV/RT$ eq. (2) | $PV/RT$ eq. (6) |
|---|---|---|---|---|
| $P = 2.8$ MPa | | | | |
| 220 | 5.750 | 2.613 | $3.611 \cdot 10^{-1}$ | $3.093 \cdot 10^{-3}$ |
| 230 | 5.677 | 2.522 | $3.042 \cdot 10^{-1}$ | $1.516 \cdot 10^{-3}$ |
| 240 | 5.640 | 2.472 | $2.539 \cdot 10^{-1}$ | $0.798 \cdot 10^{-3}$ |
| 250 | 5.544 | 2.327 | $2.099 \cdot 10^{-1}$ | $0.441 \cdot 10^{-3}$ |
| $P = 8.0$ MPa | | | | |
| 290 | 0.171 | 1.948 | 0.093 | 0.691 |
| 300 | 0.187 | 1.785 | 0.071 | 0.344 |
| 310 | 0.412 | 1.271 | 0.021 | 0.039 |
| 320 | 0.570 | 1.181 | 0.017 | 0.025 |
| 950 | 1.015 | 1.031 | 1.099 | 1.187 |
| 1000 | 1.016 | 1.029 | 1.094 | 1.181 |
| 1300 | 1.017 | 1.023 | 1.071 | 1.138 |

Comparison of these values shows that equations (1), (2), and (6) describe the character of the dependence of the coefficient of compression of $CO_2$ on temperature on the undercritical isobar (2.8 $MPa$) correctly, but quantitative deviation between the experimental and calculated data sometimes reaches several orders. In the overcritical region (8 MPa), the experimental isobar of the compression coefficient increases. None of the examined models describes this fact correctly. When the temperature is higher than the critical for $CO_2$ in 3–4 times the quantitative deviation between experimental and calculated values of $PV/RT$ is approximately equal to 5%. However the experimental function $PV/RT$ of $T$ for $CO_2$ is increasing up to 1 and all calculated functions $PV/RT$ of $T$ is decreasing to 1. For $n$-hexane and $n$-pentadecane the bond length and factor $\gamma$ are equal, respectively, to: $l = 7.9$ A and $\gamma = 4.7$; $l = 19.65$ A and $\gamma = 12.2$. The dependence of pressure on the numeral density in a system of spherecylinder for $n$-hexane and $n$-pentadecane qualitatively correlates with the experimental one. Quantitative agreement can not be obtained. The comparison between the experimental values of elastic module of $n$-hexane and $n$-pentadecane with those calculated for the hard spherecylinder model demonstrates that the model describes the behaviour of this dependence qualitatively correctly. Quantitative distinction of elastic module is large. The value of ($K_{Texper}$- $K_{Ttheor}$) increases with density for $n$-alkanes. Theoretical value of the coefficient of thermal dilatation for $n$-alkanes decreases as temperature increases both in the region of high pressures and in the region of low pressures. Experimental dependence of $\alpha_P$ on temperature is quite different: it increases with temperature under low pressures and it decreases under high pressures (see table 2).

Table 2. Coefficient of the thermal dilatation of $n$-hexane calculated on the basis of the hard spherecylinder model and obtained from the experimental results.

| | $\alpha_P \cdot 10^4$, $T^{-1}$ | | | | | |
|---|---|---|---|---|---|---|
| $P$, MPa | $T = 313$ K | $T = 313$ K | $T = 353$ K | $T = 353$ K | $T = 393$ K | $T = 393$ K |
| | exper. | theory | exper. | theory | exper. | theory |
| 0.098 | 14.00 | 11.00 | 17.10 | 10.30 | 20.90 | 9.75 |
| 49.050 | 9.76 | 10.40 | 9.64 | 9.53 | 9.49 | 8.86 |
| 98.100 | 8.18 | 10.10 | 7.46 | 9.19 | 6.65 | 8.46 |
| 47.150 | 7.09 | 9.82 | 6.27 | 8.92 | 5.39 | 8.17 |
| 196.200 | 6.39 | 9.61 | 5.52 | 8.70 | 4.59 | 7.96 |
| 245.25 | 5.73 | 9.42 | 4.93 | 8.53 | 4.09 | 7.79 |

The model of spherecylindrical particles can not be considered as appropriate for quantitative description of the coefficient of compression of $n$-alkanes. The consideration of the softness of particles in the form of (7) in this model does not lead to the improvement of correlation between the theoretical and experimental values of the coefficient of compression. The alteration of the power of repulsive force potential $n$ from 12 to 36 has no influence on the behavior and values of $PV/RT$. It can be caused by the leading role of the attractive force in the studied regions of pressures and temperatures.

## Conclusion

Comparison of the results of the calculations of elastic and thermal properties of $n$-alkanes, $CO_2$ and Ar using the models for hard and soft particles and with consideration of attraction or without it shows that equilibrium properties of liquids are determined by the geometry of molecules. The significance of the potential energy for the description of the thermodynamic properties of model system increases as temperature and density increase.

The value and the character of the dependence of elastic and thermal properties depend on the particularities of the whole potential curve (not only on its repulsive part for elastic properties and only on its attractive part for thermal properties).

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# МОДЕЛІ МАСШТАБНИХ ЧАСТОК ТА ТЕРМОДИНАМІЧНІ ВЛАСТИВОСТІ *N*-ПАРАФІНІВ

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Проаналізовано можливість використання моделей масштабних часток для опису пружних та теплових властивостей н-парафінів. Показано, що моделі масштабних часток якісно

вірно описують залежність фактора стиснення і модуля пружності від густини $n$-парафінів, при цьому кількісне розходження зростає з ростом густини. Характер залежності пружних та теплових властивостей $n$-парафінів від термодинамічних параметрів визначається особливостями всієї потенціальної кривої, а не тільки її відштовхуючої частини (для пружних властивостей) або особливостями потенціалу притягання (для теплових властивостей).