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PARTICLE-SHAPE EFFECT ON THERMOPHYSICAL PROPERTIES OF MODEL LIQUID SYSTEMS. SOLUTIONS OF HARD SPHEROCYLINDERS

Thermophysical parameters (density, adiabatic and isothermal elastic moduli, thermal expansion coefficient, and Joule–Thomson coefficient) of a solutions of hard spherocylinders with various elongations have been determined using the Monte Carlo method applied to an isothermal-isobaric ensemble characterized by the reduced temperature $T = 1.0$ and the reduced pressures $P = 1.0$ and 3.5 . It is shown that the shape of the particles, provided that their volumes are invariant, affects the thermophysical properties of the studied solutions indirectly through the free or available volume of the system, rather than the volume fraction occupied by the particles.

Keywords: Monte Carlo method, thermophysical properties, influence of particle shape, free or available volume.

1. Introduction

At the present time, we may recognize that such a direction of research as the physics of liquids and liquid systems has been formed within molecular physics [1]. The development of this direction mainly occurs through the improvement of experimental methods, in particular, neutron ones [2–4], as well as computer simulation methods, in particular, the Monte Carlo and molecular dynamics ones [5].

According to their application scope, the computer simulation methods can be divided into fundamental and applied (or engineering) ones. The purpose of applied methods is mainly to obtain the reliable and exact information about the macroscopic properties of a particle system with a known composition and a given interaction potential between the particles. The corresponding practical tasks are typical of many industries.

Nowadays, such effective computer programs as Gromax [6] and LAMMPS [7] have been created, which allow information about the thermophysical properties of specific objects to be obtained in a lot of cases without performing complicated experiments.

The reliability and accuracy of the data obtained are based on the successful choice of the “force field”, i.e. a set of parameters that characterize the interaction of atomic groups or individual atoms belonging to the same or different molecules in the researched system. Numerical values of those parameters are determined by mutually fitting the experimental and simulation results obtained for a particular macroscopic characteristic (almost always, this is the density) for a number of liquid systems selected as the “reference” ones [8]. The application value of a “force field” is determined by the transferability of its potential parameters to other liquids or liquid systems, i.e. the ability to predict the thermophysical characteristics for liquids different from the “reference” ones.

In the vast majority of works aimed at calculating the thermophysical properties of liquid systems, the matter concerns the density, self-diffusion coefficient, and shear viscosity coefficient. This circumstance makes it difficult to compare the simulation results with the experimental ones. In most cases, the self-diffusion coefficient can be determined only using the nuclear magnetic resonance and neutron experiment methods [3,9]. Due to the complicated character of the experiment, there are little relevant data. At the same time, it is not methodologically quite “hon-

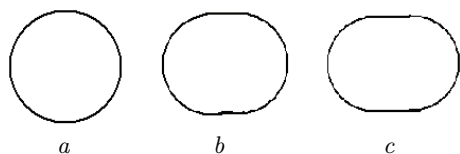


Fig. 1. Hard spherical cylinders with various elongation degrees: a hard sphere (HS) with the diameter $\sigma = 1.0$ (a); a hard spherocylinder (HSC), the diameter of the spherical surface $\sigma = 0.89$, and the length of the cylindrical surface $L = 0.23$ (b); a hard spherocylinder (HSC), the diameter of the spherical surface $\sigma = 0.84$, and the length of the cylindrical surface $L = 0.42$ (c)

est” to compare the data obtained for the density, because the model parameters are obtained exactly on their basis.

As for other parameters – in particular, the adiabatic and isothermal elastic moduli, the ultrasound propagation velocity, the thermal expansion coefficient, the Joule–Thomson coefficient, and others – the calculations of those quantities were made in a limited number of papers [10, 11]. It should be noted that the ultrasound propagation velocity is a characteristic that can be accurately and rather simply measured experimentally. Therefore, it is pertinent to use this parameter to independently evaluate that or another potential model.

The task of the fundamental direction in computer simulation is not exactly the obtaining of most accurate data for the macroscopic properties of the analyzed systems, but sooner the determination of general laws that govern the behavior of macroscopic properties of the systems with given compositions and given potentials of particle interaction. In particular, a typical challenging task is to determine the influence of the shape of molecules on the thermophysical properties of liquids and liquid systems. This effect on various thermophysical properties of individual liquids was studied earlier for a number of hard-core model systems [12–14]. However, in those works, the cited authors did not pay attention to the fact that a change in the particle shape can change the own particle volume. As a result, the reduced density of the system can also vary. In other words, the thermophysical properties were compared for the systems that actually were in different reduced states (in different phase diagram regions). The aim of this work was to elucidate the “pure” influence of the molecular shape on the thermophysical properties of liquids and their solutions.

2. Researched Object and Computer Simulation Technique

The study was performed using the model of binary solutions of hard spherical cylinders (HSCs) as an example. The characteristics of the particles of different kinds were set so that their volumes were equal to the volume of a hard sphere (HS) with a unit diameter. In Fig. 1, the models of three kinds of particles with different elongation degrees that the examined system is consisted of are presented. Accordingly, three systems of binary solutions with the concentrations $x = 0, 0.2, 0.4, 0.6, 0.8,$ and 1.0 mole fractions were studied.

Using the Monte Carlo method applied to the isothermal-isobaric ensemble [15] of systems with the total particle number $N = 216$, the following thermophysical characteristics were determined: the density, the adiabatic and isothermal elastic moduli, the thermal expansion coefficient, and the Joule–Thomson coefficient. The corresponding calculations were performed using dimensionless variables for which the hard sphere diameter σ was selected as the length unit, the particle mass m was the mass unit, and the quantity $\sqrt{k_B T/m}$, where k_B is the Boltzmann constant and T the temperature, was the velocity unit [16].

In a system of hard particles, the density depends on the parameters P and T via their ratio so that the thermodynamic state of the system is also determined by this ratio. In the selected system of length, mass, and velocity units, $P/T = k/\sigma^3$. The calculations were carried out for the reduced P/T ratio with values of 1.0 and 3.5 . It is convenient to talk about them as about calculations for the reduced temperature $T = 1.0$ and the reduced pressures $P = 1.0$ and 3.5 .

Four types of a new configuration generation were used at simulation: the displacement of a molecule as a whole, the rotation of a molecule at a random angle around its center of mass, a change of the particle kind, and a change of the main cell volume. The maximum displacement, maximum rotation angle, and maximum volume change were selected so that the corresponding fraction of accepted configurations was 30% [12].

The Vega algorithm [17] was applied to calculate the distance between the surfaces of spherical cylinders. The generated sequence of system configurations was used to find the mean and root mean square

fluctuations of the system volume. To estimate the error of the calculated values, the total sequence of configurations was divided into 10 subsequences, and the average values of the volume and other quantities were calculated for each of them. Then, the average value and the random error were determined for a set of 10 “measurements”.

The density ρ and the isothermal elastic modulus K_T were calculated according to the formulas [18]

$$\rho = \frac{N}{\langle V \rangle}, \quad (1)$$

where N is the number of particles, and $\langle V \rangle$ is the average cell volume, and

$$K_T = \frac{T \langle V \rangle}{\langle \Delta V^2 \rangle}, \quad (2)$$

where T is the temperature, and $\langle \Delta V^2 \rangle$ is the mean square fluctuation of the cell volume. Since the potential energy in the system of hard particles is zero, the expressions for calculating the thermal expansion coefficient α_p and the isobaric heat capacity C_P are simpler in comparison with the general case:

$$\alpha_p = \frac{P}{TK_T}, \quad (3)$$

where P is the pressure, and

$$C_P = C_V + P \langle V \rangle \alpha_p. \quad (4)$$

Here, C_V is the isochoric heat capacity, which equals $\frac{3}{2}N$ for N hard spheres, $\frac{5}{2}N$ for N hard spherical cylinders, and $\frac{3}{2}N_1 + \frac{5}{2}N_2$ for a mixture of N_1 hard spheres and N_2 hard spherical cylinders.

The obtained data were used to calculate the ratio γ between the isobaric and isochoric heat capacities, the adiabatic elastic modulus

$$K_S = K_T \left(1 + \frac{P \langle V \rangle \alpha_p}{C_V} \right), \quad (5)$$

and the Joule–Thomson coefficient

$$\mu_{JT} = \left(\frac{\partial T}{\partial P} \right)_H = \frac{\langle V \rangle}{C_P} [T \alpha_p - 1], \quad (6)$$

where H is the enthalpy.

3. Results of Calculations

The concentration dependences of the researched thermophysical quantities are shown in Figs. 2, 3, and 5 to 7. As one can see from Fig. 2, the density of binary solutions of hard spherical cylinders does not depend on the concentration. The densities of both individual systems of hard spheres (HSs) and hard spherical cylinders (HSCs) with various particle elongation degrees, as well as their mutual solutions, are identical at the fixed pressure and temperature. Therefore, provided that the particle volumes are the same, the particle shape does not affect the solution density.

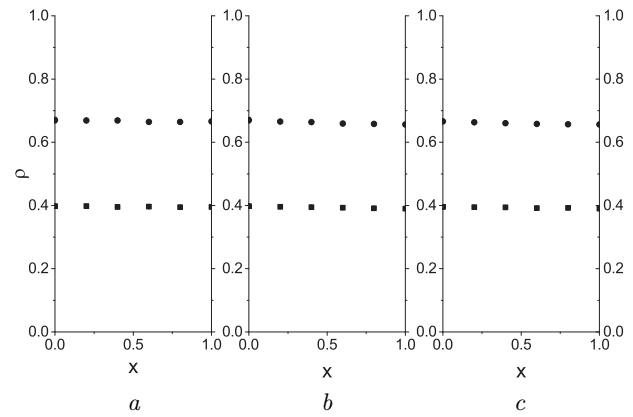


Fig. 2. Concentration dependences of the binary HSC solution density ρ : the HS-HSC system with $L/\sigma = 0.25$ (a); the HS-HSC system with $L/\sigma = 0.50$ (b); the HSC system with $L/\sigma = 0.25$ (c) and 0.50. $P = 1.0$ (■) and 3.5 (●)

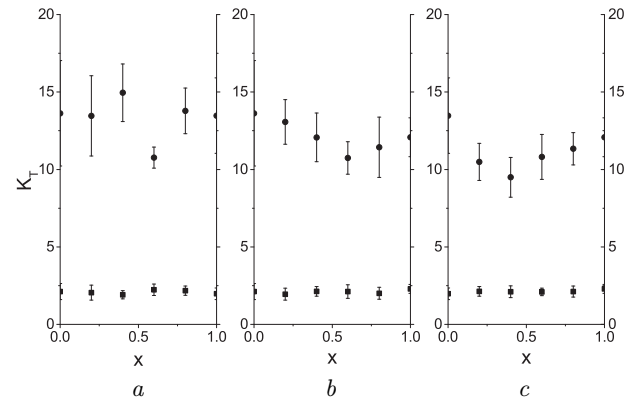


Fig. 3. Concentration dependences of the isothermal elastic modulus K_T for binary HSC solutions: the HS-HSC system with $L/\sigma = 0.25$ (a); the HS-HSC system with $L/\sigma = 0.50$ (b); the HSC system with $L/\sigma = 0.25$ (c) and 0.50. $P = 1.0$ (■) and 3.5 (●)

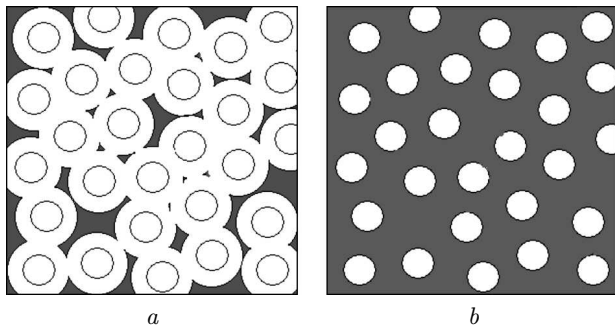


Fig. 4. The accessible or free volume (grey-colored, *a*) and the volume not occupied by the particles (grey-colored, *b*) in a system of hard disks

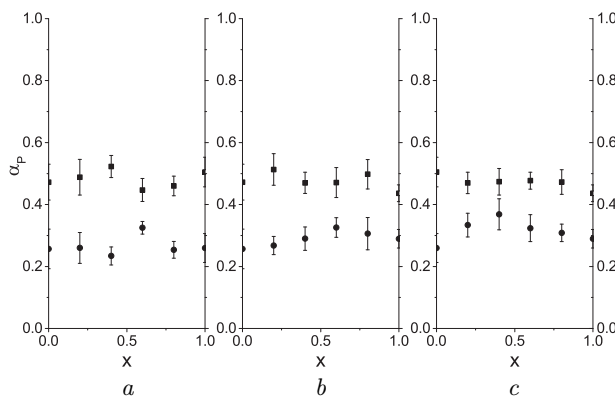


Fig. 5. Concentration dependences of the thermal expansion coefficient α_p for binary HSC solutions: the HS-HSC system with $L/\sigma = 0.25$ (*a*); the HS-HSC system with $L/\sigma = 0.50$ (*b*); the HSC system with $L/\sigma = 0.25$ (*c*) and 0.50 . $P = 1.0$ (■) and 3.5 (●)

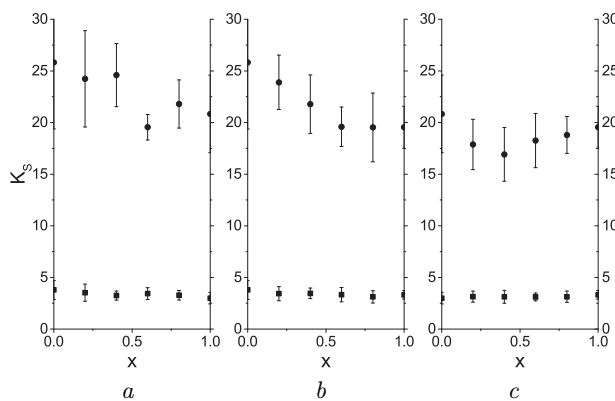


Fig. 6. Concentration dependences of the adiabatic elastic modulus K_S for binary HSC solutions: the HS-HSC system with $L/\sigma = 0.25$ (*a*); the HS-HSC system with $L/\sigma = 0.50$ (*b*); the HSC system with $L/\sigma = 0.25$ (*c*) and 0.50 . $P = 1.0$ (■) and 3.5 (●)

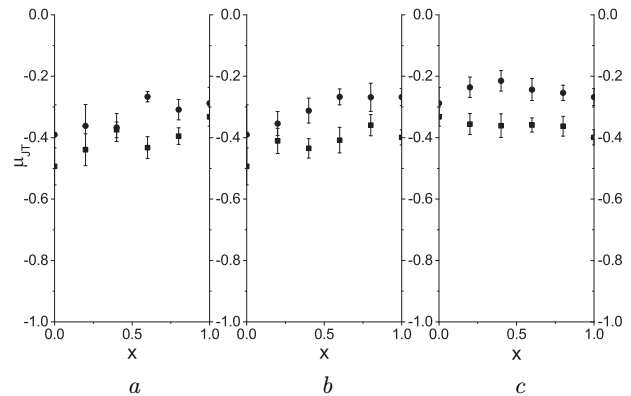


Fig. 7. Concentration dependences of the Joule–Thomson coefficient μ_{JT} or binary HSC solutions: the HS-HSC system with $L/\sigma = 0.25$ (*a*); the HS-HSC system with $L/\sigma = 0.50$ (*b*); the HSC system with $L/\sigma = 0.25$ (*c*) and 0.50 . $P = 1.0$ (■) and 3.5 (●)

Concerning the isothermal elastic modulus, its thermodynamic behavior is more complicated. At low pressures ($P = 1.0$), the K_T -values for the HS solutions and the HSC solutions with various particle elongation degrees almost do not depend on the solution composition (Fig. 3).

As the pressure increases ($P = 3.5$), some decrease of the elastic modulus is observed for those systems in which particle shapes more deviate from the spherical one (Fig. 3, *c*). In particular, for most solutions of the HS–HSC system with the ratio $L/\sigma = 0.25$, the value of K_T is close to 14 (Fig. 3, *a*), whereas, for the solutions of the same system with the ratio $L/\sigma = 0.5$, the value of K_T is close to 12 (Fig. 3, *b*). For most solutions of the HSC system with various particle elongation degrees, the value of K_T is close to 10 (Fig. 3, *c*).

A specific feature in the concentration dependence of the isothermal elastic modulus of the systems with the most elongated spherical cylinders is the presence of a minimum in the concentration interval near $x \sim 0.6$. Therefore, at such concentrations, the solution can be compressed more easily, which testifies to its more “loose” structure. Since the particle volumes are identical, this feature cannot be explained by the difference in the packing coefficients, i.e. the fraction of the system volume occupied by the particles themselves.

In this regard, it is reasonable to refer to the concepts of the excluded and free volumes introduced by Van der Waals [19]. The excluded volume is the part of the system volume, where the center of mass of a

particle cannot be placed without the overlapping of the latter with neighbor particles. According to Van der Waals, for the loose systems of particles with a hard core, the excluded volume is equal to four times the volume of the particles themselves and coincides with the volume correction in the equation named after him. The part of the system volume, where the center of mass of a particle can be placed without the overlapping with other particles is called either free [20] or accessible [21] volume. In book [22], the concepts of free and accessible volumes are used as synonyms. The difference between the free (or accessible) volume and the volume not occupied by particles is illustrated in Fig. 4.

The ability to compress the system is evidently associated with the presence of such regions, where the particle can move, i.e. with the presence of the free or accessible volume. The difference between the K_T values for the solutions of elongated particles and the solutions of spherical particles testifies to the difference between the free volumes in those systems. In our case, this means that the free volume of the elongated particle system is larger than that of the spherical particle system. Qualitatively, this result can be explained by the fact that an elongated particle can more likely be “squeezed” into the system by “rotating” it, i.e. finding an orientation in which it does not overlap with the neighbors. For spherical particles, such a possibility is absent.

As for the thermal expansion coefficient α_p , its value decreases with the increasing pressure for all three systems (Fig. 5). At low pressures, α_p is almost independent of x for all solutions. At high pressures, the concentration dependence of the thermal expansion coefficient has peculiarities at the same concentrations of elongated spherical cylinders as K_T has. Namely, α_p of solutions with $x \sim 0.4 \div 0.6$ exceeds the corresponding values of α_p for one-component liquids. This effect can also be explained by the growth of the free volume in the solution as compared with that in one-component systems.

The concentration dependence of the adiabatic elastic modulus K_S is similar to that of the isothermal elastic modulus (Fig. 6). The only difference consists in their magnitudes.

Figure 7 exhibits the concentration dependences of the Joule–Thomson coefficient. As one can see, within the determination error, the dependence $\mu_{JT}(x)$ is close to linear. The pressure growth from $P = 1.0$

to $P = 3.5$ leads to the increase of the Joule–Thomson ratio from -0.4 to -0.2 . The negative μ_{JT} -values mean that, at all pressure and concentration values, the liquid temperature increases under adiabatic throttling conditions (the slow gas flow through a porous partition).

4. Main Results and Conclusions

1. The Monte Carlo method is applied to the isothermal-isobaric ensemble in order to determine the set of thermophysical parameters of the liquids consisting of particles with various shapes (the elongation degree), namely, hard spherical cylinders. In order to distinguish the influence of the particle form on the thermophysical properties, the researched systems were assumed to be in the same reduced state, i.e. the shape of the particles was changed, but their volume was left constant.

2. An analysis of the thermophysical characteristics of binary solutions of hard spherical cylinders shows that those parameters are determined by the free (or accessible) volume of the examined systems, rather than the particle packing coefficient.

3. The influence of the particle shape on the thermophysical properties of the studied solutions provided the constancy of particle volume is carried out indirectly by means of the free or accessible volume parameter. In this connection, it is shown that, when studying the influence of particle shape on the thermophysical properties of both model systems and real molecular solutions, just the free or accessible volume parameter is pertinent to be applied.

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ВПЛИВ ФОРМИ ЧАСТИНОК НА ТЕПЛОФІЗИЧНІ ВЛАСТИВОСТІ МОДЕЛЬНИХ РІДИННИХ СИСТЕМ. РОЗЧИНИ ТВЕРДИХ СФЕРОЦИЛІНДРІВ

Методом Монте-Карло в ізотермічно-ізобаричному ансамблі визначено теплофізичні характеристики систем твердих сфероциліндрів різного ступеня видовженості: густину, адіабатичний та ізотермічний модулі пружності, коефіцієнт теплового розширення та коефіцієнт Джоуля-Томсона за приведеної температури $T = 1,0$ та приведених тисків $P = 1,0$ і $3,5$. Показано, що вплив форми частинок за умови сталості їх об'єму на теплофізичні властивості досліджених розчинів здійснюється опосередковано не через коефіцієнт пакування частинок, а через вільний або доступний об'єм.

Ключові слова: метод Монте-Карло, теплофізичні властивості, вплив форми частинок, вільний або доступний об'єм.