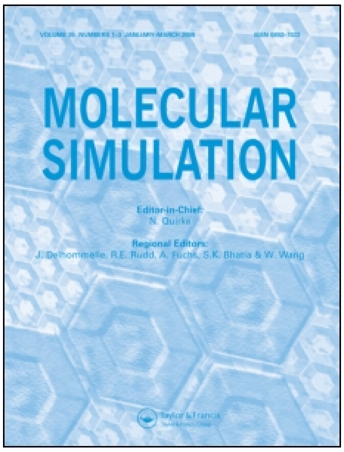

Molecular Simulation
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

Monte Carlo Simulations on Mixtures of the Kihara Point-wise and Rod-like Molecules

Ryszard Kantor[a]; Tomášk Boublík[a]
[a] Institute of Chemical Process Fundamentals, Czechoslovak Academy of Sciences, Prague 6, Czechoslovakia

To cite this Article Kantor, Ryszard and Boublík, Tomášk(1989) 'Monte Carlo Simulations on Mixtures of the Kihara Point-wise and Rod-like Molecules', Molecular Simulation, 2: 3, 217 — 221

To link to this Article: DOI: 10.1080/08927028908031370

URL: http://dx.doi.org/10.1080/08927028908031370

Molecular Simulation, 1989, Vol. 2, pp. 217–221
Reprints available directly from the publisher
Photocopying permitted by license only

MONTE CARLO SIMULATIONS ON MIXTURES OF THE KIHARA POINT-WISE AND ROD-LIKE MOLECULES

RYSZARD KANTOR and TOMÁŠ BOUBLÍK

Institute of Chemical Process Fundamentals, Czechoslovak Academy of Sciences, 165 02 Prague 6, Czechoslovakia

(*Received May, 1988; in final form August, 1988*)

Simulations by the Monte Carlo method were performed on an equimolar mixture of the Kihara molecules with the point-wise and rod-like cores. Values of the compressibility factor and internal energy for five equilibrium points were obtained as well as the excess properties for the studied mixtures.

KEY WORDS: Mixture, Kihara fluids, compressibility factor, internal energy, excess properties.

INTRODUCTION

At present the Kihara potential appears to be a very convenient model to characterize pair interactions in pure molecular fluids and their mixtures. The main reason for its application is a simple mathematical formalism involved in the derivation of expressions for the thermodynamic functions and the possibility to treat spherical and nonspherical molecule fluids in a uniform way. Perturbation theory for the Kihara fluids was developed in this laboratory [1, 2].

Recently we performed Monte Carlo (MC) simulations for the simplest Kihara nonspherical model – the rod-like molecules [3]. Results of the perturbation expansion have been in good agreement with the obtained experimental data. As a continuation of the recent studies we performed MC simulations for the equimolar mixture of Kihara spherical and nonspherical molecules. These results may serve as a background for testing perturbation theories of mixtures and the applicability of the Kihara model to predict excess properties of real fluids.

THE MODEL OF INTERMOLECULAR POTENTIAL

We studied the equilibrium behaviour of the equimolar mixture of the Kihara molecules with point-wise and rod-like cores. All three types of pair interactions in the binary mixture were described by the 12-6 potential

$$u(s) = 4\varepsilon\,[(\sigma/s)^{12} - (\sigma/s)^{6}] \tag{1}$$

where ε is the depth of the minimum of the pair potential and s is the shortest distance between cores of interacting molecules. Similarly to our recent study of a pure fluid [3] we kept constant the ratio between rod length, l, and the parameter σ,

$$\gamma = (l + \sigma)/\sigma = 2 \qquad (2)$$

for the rod-like molecules.

DETAILS OF EXPERIMENTS

Our experiments were performed in an NVT ensemble with N = 144 molecules in a cubic box of side L with periodic boundary conditions. For the given type of molecular pair we calculated contributions to statistical averages up to distance s_{ij}

$$s_{ij} = [L - (\gamma_i - 1)\sigma - (\gamma_j - 1)\sigma]/2 \qquad (3)$$

where $\gamma_1 = 1$ (point core) and $\gamma_2 = 2$ (rod-like molecule). The transition probabilities along the Markovian chain were, however, determined for continuous potential, $u'(s)$, truncated at the distance s_{22} (the shortest of the s_{ij} distances)

$$\begin{aligned} u'(s) &= u(s) - u(s_{22}) \qquad s < s_{22} \qquad (4)\\ u's) &= 0 \qquad\qquad\qquad\; s \geqslant s_{22} \end{aligned}$$

The minimum value of the distance s_{22} amounts to $2.33\,\sigma$; one can thus expect that the truncation of the potential affects the determined structure of the studied system only very slightly. The standard MC technique was used; one step of the simulation procedure consisted of the following steps:

1) One molecule (regardless of its type whether point-wise or rod-like) was selected at random

2a) If the selected molecule was Lennard-Jones (LJ) molecule, then translation was performed

2b) If the selected particle was a rod-like molecule, then alternately translation or rotation was performed.

The maximum translational and rotational displacements of particles were adjusted to such values, that approximately one half of newly generated configurations in each of the above steps was accepted (according to the standard Metropolis criterion [4]).

After each 5N configurations the following quantities were recorded: the order parameter [5, 6], number of pairs with the given surface-to-surface distances (3 types of pairs) and the dependence of the canonical average of scalar product $\langle \vec{r}\vec{v} \rangle_s$ on the shortest surface-to-surface distance – the last quantity only for the rod-point and rod-rod pairs; for the point-point pairs it holds

$$\langle \vec{r}_{11}\vec{v} \rangle_s = |\vec{r}_{11}| \qquad (5)$$

Our main interest was focussed on the thermodynamic behaviour rather than on the structural properties. We therefore calculated the canonical averages of functions

$$w_l = \sum_{k<l} u_{kl}(s) \qquad (6)$$

(over all configurations) and

$$w_2 = \sum_{k<l} \left[\frac{du(s)}{ds} (\vec{r}\vec{v}) \right]_{kl} \qquad (7)$$

over 5N step configurations. The summations in (6) and (7) are considered for all pairs (in one configuration) with distances $s < s_{ij}$. The calculation of internal energy is then straightforward:

$$U = \langle w_1 \rangle; \qquad (8)$$

from the virial theorem we obtained pressure, p,

$$pV = NkT - \langle w_2 \rangle / 3 \qquad (9)$$

It was convenient to use the equilibrium configuration of hard spheres and spherocylinders found in [7] as an initial configuration of the present simulations. For each equilibrium point we generated at least 950 000 configurations, the initial fraction of 200 000 configurations was discarded.

RESULTS AND DISCUSSION

From the recorded numbers of pairs $\langle N_{ij}^{av}(s) \rangle$ in given intervals $(s - \Delta s/2, s + \Delta s/2)$

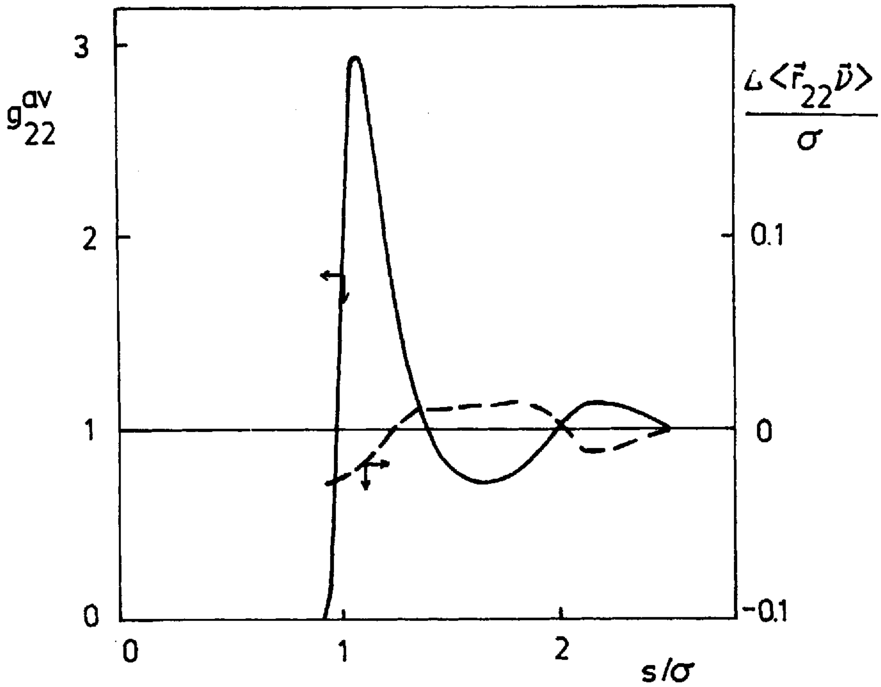

Figure 1 The average pair correlation function $g_{22}^{av}(s)$ (for the pair rod-rod) and the dependence of $\Delta\langle \vec{r}_{22}\vec{v}\rangle_s$ on the surface-to-surface distance. Both functions are given at the temperature $T^* = 1.0$ and packing fraction $y = 0.3885$.

Table 1 Compressibility factor, internal energy, heat capacity, and the excess properties of the equimolar mixture of point-wise and rod-like molecules (V_{mix} is the volume of the mixture. The packing fractions, y, corresponds to the equimolar mixture of hard spheres and spherocylinders with thickness $\sigma/2$).

kT/ε	y	pV/NkT	$-U/N\varepsilon$	c_V/Nk	$\Delta V_{mix}/V_{mix}$	$\Delta H_{mix}/N\varepsilon$
0.70	0.4453	1.52 ± 0.05	5.334 ± 0.006	1.18	0.001	0.35
1.00	0.4453	3.46 ± 0.09	5.019 ± 0.008	1.04	0.005	0.30
1.00	0.3885	1.45 ± 0.03	4.419 ± 0.004	0.70	0.011	0.37
1.00	0.3368	0.48 ± 0.04	3.818 ± 0.004	0.57	−0.026	0.37
1.35	0.4453	4.39 ± 0.05	4.696 ± 0.009	0.88	0.004	0.24

of surface-to-surface distances we calculated the angle averaged pair correlation function, $g_{ij}^{av}(s)$, [7] from simple formulas:

$$\langle N_{ij}^{ss}(s)\rangle = \frac{N_i N_j}{V} g_{ij}^{av}(s)\, S_{i+s+j}\, \Delta s \quad (i \neq j) \tag{10}$$

and

$$\langle N_{ii}^{ss}(s)\rangle = \frac{N_i(N_i - 1)}{2V} g_{ii}^{av}(s)\, S_{i+s+i}\, \Delta s \tag{11}$$

S_{i+s+j} is the surface of a combined body formed by the centre of body j when it is moved around body i with the constant surface-to-surface distance s.

A typical example of the functions $g_{ii}^{av}(s)$ is depicted in Figure 1. This figure shows also the dependence of the function

$$\Delta\langle \vec{r}_{ij}\vec{v}\rangle_s = \langle \vec{r}_{ij}\vec{v}\rangle_s - \langle \vec{r}_{ij}\vec{v}\rangle_s^* \tag{12}$$

on the surface-to-surface distance. The asterisk denotes the exactly known low density limit

$$\langle \vec{r}_{ij}\vec{v}\rangle_s^* = 3V_{i+s+j}/S_{i+s+j} \tag{13}$$

where V_{i+s+j} is the volume of the combined body. The difference represented by equation 12 is always small and vanishes at distances greater than those corresponding to the first peak on the $g_{ij}^{av}(s)$ function.

The calculated values of the compressibility factor and internal energy for 5 equilibrium points are given in Table 1. The calculated values contain the perturbation contributions correcting the truncation of the summations at $s = s_{ij}$:

$$\Delta U = \sum_{i,j=1}^{2} x_i x_j \frac{N^2}{2V} \int_{s_{ij}} u(s)\, g_{ij}^{av}(s)\, S_{i+s+j}\, ds \tag{14}$$

$$\Delta(pV) = -\sum_{i,j=1}^{2} x_i x_j \frac{N^2}{6V} \int_{s_{ij}} \frac{du(s)}{ds}\, g_{ij}^{av}(s)\, \langle \vec{r}_{ij}\vec{v}\rangle_s S_{i+s+j}\, ds \tag{15}$$

(V is the volume of the system studied). Experimental errors were calculated from the recorded subaverages of functions (6) and (7) along the Markovian chain. In Table 1. values of c_V/Nk are also listed. These values were calculated from the recorded fluctuations in internal energy; the estimated error amounts to approximately 15 per cent.

EXCESS FUNCTIONS FOR THE STUDIES MIXTURE

Our present values of the internal energy and compressibility factor for the Kihara mixtures made it possible to calculate the excess properties. We calculated them at temperatures and pressures given in Table 1. Properties of the pure rod-like fluid were obtained from our recent simulations [3] combined with the perturbation theory, thermodynamical functions of the LJ fluid we calculated from the equation of Nicolas *et al.* [8]. It can be seen, that the excess volume is practically zero, as for hard body mixtures. The excess enthalpy is relatively high and positive (see Table 1). The estimated error in the excess enthalpy calculated as the combined errors of the MC values of the mixture and pure components amounts less then 10 per cent whereas that of the excess volume, where the size of the studied system plays an important role, cannot be determined.

CONCLUSIONS

We simulated the equilibrium behaviour of equimolar mixture of Kihara point-core molecules and rod-like molecules ($\gamma = 2$) for five equilibrium points. Some structural properties as well as the excess properties of the studied mixtures were obtained. We believe, that our data will prove to be useful for further studies of the Kihara fluid.

References

[1] T. Boublik, "Perturbation theory for fluids of rod-like molecules interacting via the Kihara potential," *Mol. Phys.*, **32,** 1737 (1976).
[2] J. Pavlíček and T. Boublik, "Vapour-liquid equilibrium at elevated pressures from the perturbation theory. I. One-component systems," *Fluid Phase Equil.*, **7,** 1 (1981).
[3] R. Kantor and T. Boublik, "Monte Carlo study of the Kihara rod-like molecule systems," *Czech. J. Phys.*, **B38,** 321 (1988).
[4] N. Metropolis, A.W. Rosenbluth, M.N. Rosenbluth, A.H. Teller and E. Teller, "Equation of state calculation by fast computing machines," *J. Chem. Phys.*, **21,** 1087 (1953).
[5] P.G. De Gennes, "Short range order effect in the isotropic phase of nematics and cholesterics," *Crystals Liq. Crystals*, **12,** 1087 (1953).
[6] T. Boublík, I. Nezbeda and O, Trnka, "Monte Carlo study of hard spherocylinders," *Czech. J. Phys.*, **B26,** 1081 (1976).
[7] T. Boublík and I. Nezbeda, "Monte Carlo study of the equimolar mixture of hard spheres and spherocylinders," *Czech. J. Phys.*, **B30,** 121 (1980).
[8] J.J. Nicolas, K.E. Gubbins, W.B. Street and D.J. Tildesley, "Equation of state for the Lennard-Jones fluid," *Mol. Phys.*, **37,** 1429 (1979).