A Molecular Dynamics Simulation of Pressure Induced Liquid-Plastic Phase Transition of Pure Cyclohexane and Cyclohexane in Silica Cavities

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A MOLECULAR DYNAMICS SIMULATION OF PRESSURE INDUCED LIQUID-PLASTIC PHASE TRANSITION OF PURE CYCLOHEXANE AND CYCLOHEXANE IN SILICA CAVITIES

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Molecular dynamics simulations at temperature 313 K and pressures up to 4 kbar for six-centre Lennard-Jones model of C_6H_{12} are reported. The calculations are performed for pure cyclohexane and cyclohexane in pores. A cavity is obtained by placing silica clusters at the corners of a cubic box. Two cavities of diameter of about 30 Å and 50 Å are considered. Thermodynamic, structural and dynamic properties of molecule confined to the pores are compared with the results for pure cyclohexane. Changes of molecular behaviour with diminishing pore size are observed and the liquid-plastic transition point shifts to higher pressures.

KEY WORDS: Liquid-plastic, phase transition, cyclohexane, silica cavities

INTRODUCTION

The phase transition of cyclohexane was studied experimentally for wide range of temperatures and pressures up to 3 kbar by Würflinger [1] and Wisotzki and Würflinger [2]. Recently, the molecular dynamics (MD) simulation method was used to investigate thermodynamic and transport properties of pure cyclohexane at high temperatures [3]. It was found that MD calculations realistically predict the transition to the high-temperature rotator phase. Our earlier studies [4, 5] concentrated on MD simulations of the liquid-plastic phase transition of cyclohexane for densities corresponding to the experimental data at atmospheric pressure. We considered pure cyclohexane [4] and cyclohexane in small cavities [5]. For pure cyclohexane we obtained satisfactory agreement between calculated heat capacities, diffusion coefficients, rotational and angular velocity correlation times and experimental data. In the case of cyclohexane in small pores we observed supercooling and depression of the transition point in comparison to the bulk phase. These results matched quite well experimental data for cyclohexane in porous silica [6–8].

To our knowledge high pressure measurements of cyclohexane in a restricted space, e.g. in pores of sol-gel glass, have not been peformed. This paper constitutes an attempt to study the pressure induced liquid-plastic phase transition of cyclohexane in modelled porous medium using MD simulation in the microcanonical ensemble (NVE). To get information on how the restricted geometry

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affects molecular dynamics and particularly the liquid-plastic phase transition the calculations were performed for cyclohexane in the pure phase and in two cavities of diameters of about 30 Å and 50 Å. Each simulation started from the fcc structure, characteristic for the plastic phase, and we studied the ability of the system to melt the initial configuration. From the MD simulation results diffusion coefficients, rotational relaxation times and correlation times of the angular velocities were calculated. We also studied thermodynamic and structural properties of the cyclohexane molecules.

SIMULATION METHOD

The molecular dynamics simulation of pure cyclohexane was identical to our previous paper [4]. We considered a set of 108 molecules in a cubic box and periodic boundary conditions were applied. The cyclohexane molecule was a single rigid unit with fixed bond lengths and fixed bond angles, and it was modelled by six Lennard-Jones (LJ) sites placed at the centres-of-mass of CH_2 groups in the chair form [9]. The chair isomer was chosen because it is more stable than the twist-boat form by about 23 kJ/mol [10, 11] and at the room temperature only 0.1% or less cyclohexane molecules exist in the twist-boat conformational state [11]. The parameters for C_6H_{12} molecule are collected in table 1. To calculate the forces we considered neighbouring LJ sites inside a sphere of radius $3\sigma_{cc}$ and shifted force potential [12]. The equations of motions were solved using the predictor-corrector method [13], fifth-order for translations and fourth-order for rotations (quaternions and angular velocities). The calculations were carried out for time-step of 5 fs. The initial configuration of the cyclohexane molecules was an fcc structure and random orientations were assigned. Initial translational and angular velocities were chosen randomly from a uniform distribution in such a way that they were consistent with the required temperature, and resultant momentum of the whole system was zero. During 2000 time-steps (10 ps) of the equilibration run velocities were scaled to obtain the required temperature. Then the system relaxed through the next 8000 time-steps (40 ps), and the running averages of thermodynamic quantities such as temperature, pressure and energies were calculated.

To study the dynamics of cyclohexane in porous silica we adopted the cavity model described in Reference [5]. Initially 108 or 256 molecules were placed in a cubic box at locations of the fcc lattice, and than 13 molecules from the centre

Table 1 Structure of C_6H_{12} and LJ potential parameters.

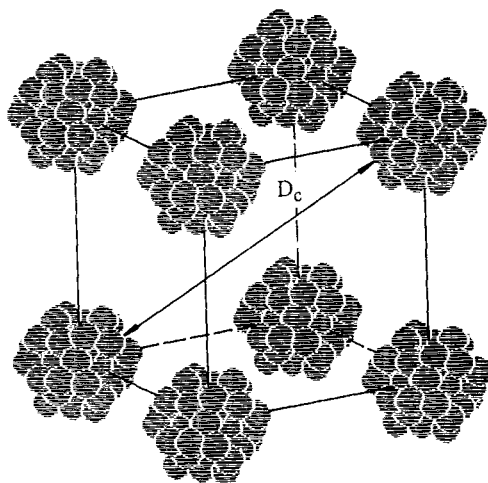| *Structure of cyclohexane*	
CH_2-CH_2 distance	1.64 Å
CH_2-CH_2-CH_2 angle	108.43^0
Inertia moments: I_x	$194.3 \cdot 10^{-48}$ kgm^2
I_z	$340.0 \cdot 10^{-48}$ kgm^2
LJ potential parameters	
cyclohexane: ε_{cc}/k_B	61.8 K
σ_{cc}	3.851 Å
oxygen: ε_{oo}/k_B	230 K
σ_{oo}	3.0 Å

Figure 1 The translated box with the silica microspheres at its corners. The space between the silica clusters represents cavity of diameter D_c.

of the box were replaced by a rigid silica cluster of 12 Å diameter. The cluster was cut from amorphous silica whose structure was simulated using the melt-quench technique [14, 15]. Applying periodic boundary conditions one obtained a lattice of the silica microspheres, and the simulation box with the silica cluster at its centre is equivalent to the translated box with the silica clusters at its corners. The translated box is shown in figure 1 and the space between the clusters represents a cavity of diameter D_c. This diameter may be estimated as follows

$$D_c = \sqrt{3} \, L - d_c, \tag{1}$$

where L is the side of the cubic box and d_c is the diameter of the silica cluster.

We considered two systems: a small system with 95 cyclohexane molecules and a large one with 243 molecules. Our calculations were carried out for $T = 313.4$ K and experimental densities of pure cyclohexane obtained for pressure up to 4 kbar [2], see table 2. The box length, L, was changed with density and the cavity diameter D_c decreased from 34 Å to 31 Å for the small system and from 50 Å to 46 Å for the large one for pressures raising from 1 bar to 4 kbar. In interaction cyclohexane-silica we took into account only oxygen atoms because of small size of silicon and its small polarizability [16]. The cyclohexane-oxygen interaction was represented by LJ potential and the potential parameters were calculated using the Lorentz-Berthelod mixing rulers [12]. The LJ potential parameters for oxygen were identical as those used before to describe non-bridging oxygens [15], and they are presented in table 1. The potential well depth is larger than the usual value for oxygen [12]. ε_{00} was estimated using the Kirkwood-Mueller formula [17] and parameters (polarizability, diamagnetic susceptibility and van der Waals' radius) for oxygen employed in the study of zeolites [16, 18]. The large values of polarizability and susceptibility in comparison with those for oxygen in molecules like O_2 or CO_2 [18] explains the differences in the potential well depths. To keep the silica cluster

Table 2 Thermodynamic properties of considered systems.

ρ (g/cm^3)	p^{exp} (kbar)	T^{MD} (K)	p^{MD} (kbar)	$U_{conf}{}^{MD}$ (kJ/mol)	$E_{tot}{}^{MD}$ (kJ/mol)
Bulk					
0.7591	0.001	306.7	0.11	-29.707	-22.056
0.7846	0.3	313.4	0.46	-30.655	-22.839
0.8036	0.6	311.4	0.69	-31.598	-23.830
0.8354	0.7	312.2	1.26	-32.831	-25.043
0.8484	0.9	313.4	1.87	-33.008	-25.192
0.8588	1.2	315.5	2.23	-33.282	-25.412
0.8680	1.5	319.4	2.55	-33.541	-25.575
0.8812	2.0	307.3	2.94	-33.806	-26.140
0.8930	2.5	308.2	3.63	-34.054	-26.366
0.9037	3.0	311.7	4.22	-34.254	-26.478
$D_c \cong 50$ Å					
0.7591	0.001	316.1	0.20	-30.489	-22.603
0.7846	0.3	312.0	0.54	-31.599	-23.818
0.8036	0.6	305.3	0.87	-32.398	-24.783
0.8354	0.7	312.7	1.67	-33.349	-25.549
0.8484	0.9	307.2	2.06	-33.741	-26.078
0.8588	1.2	314.8	2.60	-33.966	-26.114
0.8680	1.5	311.6	3.00	-34.126	-26.355
0.8812	2.0	305.8	3.44	-34.417	-26.791
0.8930	2.5	310.4	4.10	-34.636	-26.894
0.9037	3.0	316.6	4.70	-34.887	-26.990
0.9140[a]	3.5	308.3	4.98	-35.234	-27.544
0.9234[a]	4.0	310.8	5.50	-35.317	-27.566
0.7591	0.001	312.6	0.23	-31.898	-24.097
0.7846	0.3	309.8	0.67	-32.808	-25.080
0.8036	0.6	304.0	0.94	-33.828	-26.171
0.8354	0.7	315.9	1.82	-34.837	-26.957
0.8484	0.9	306.1	2.28	-35.164	-27.530
0.8588	1.2	317.2	2.80	-35.285	-27.373
0.8680	1.5	312.3	3.12	-35.588	-27.798
0.8812	2.0	312.4	3.70	-35.879	-28.087
0.8930	2.5	310.0	4.30	-36.166	-28.432
0.9037	3.0	312.8	4.95	-36.238	-28.436
0.9140[a]	3.5	316.9	5.62	-36.598	-28.495
0.9234[a]	4.0	305.4	6.04	-36.600	-28.983

[a] The densities extrapolated from data of Reference [2]

unmoved during the simulation the forces and torques acting on the silica cluster were set to zeroes. Moreover, the centre-of-mass of the cyclohexane molecule set was not translated to the centre of the simulation box. The remain details of the simulation method were the same as for bulk cyclohexane.

RESULTS AND DISCUSSION

Thermodynamic properties

Table 2 presents average values of temperature, T^{MD}, pressure, p^{MD}, and the configurational and total energies, $U_{conf}{}^{MD}$ and $E_{tot}{}^{MD}$, calculated during the molecular

dynamics simulations for bulk cyclohexane and C_6H_{12} in the cavities. The average temperature was calculated from the kinetic energy of cyclohexane molecules and pressure was estimated using the virial theorem [12]. The configurational energy was calculated as an average value of the potential energy and the total energy, E_{tot}^{MD}, was obtained as a sum of the configurational and kinetic energies. In the case of cyclohexane in the cavities the potential energy and virial arising from C_6H_{12}-silica interactions were taken into account.

The maximum fluctuations in the quantities collected in table 2 were observed at the highest density. For temperature, pressure and the energies U_{conf}^{MD} and E_{tot}^{MD} they were 10 K, 0.19 kbar, 0.24 kJ/mol and 8 J/mol, respectively, for bulk system, 8 K, 0.13 kbar, 0.17 kJ/mol and 6 J/mol for the large cavity and 10 K, 0.21 kbar, 0.27 kJ/mol and 9 J/mol for the small cavity. No drifts of the total energy and temperature were observed.

For the pure system, for three lowest densities, where bulk cyclohexane exists as a liquid, the pressures obtained from simulations are consistent with the experimental values, compare figure 2. For higher densities, where cyclohexane forms the plastic phase, density dependence of simulated and experimental pressures is almost the same, but the computed pressures are off by about 1 kbar. In the presented calculations the cyclohexane molecule was treated as a rigid unit. This approximation does not allow to distort the molecular frame, which may appear in real system, and it may lead to larger values of the calculated pressures, particularly at higher densities. In the liquid and plastic phases the total and configurational energies decrease with increasing density at different rates; in the liquid state one observes faster decrease of the energies than in the plastic phase.
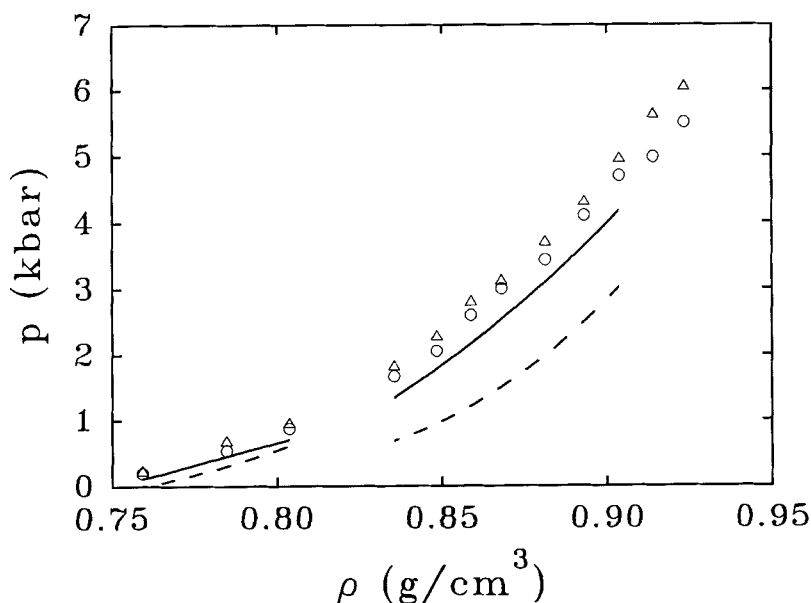

Figure 2 Density dependence of pressure for pure cyclohexane (solid lines) and cyclohexane in the large cavity, $D_c \cong 50$ Å, (circles) and in the small cavity, $D_c \cong 30$ Å, (triangles). The broken lines represent the experimental pressure [2].
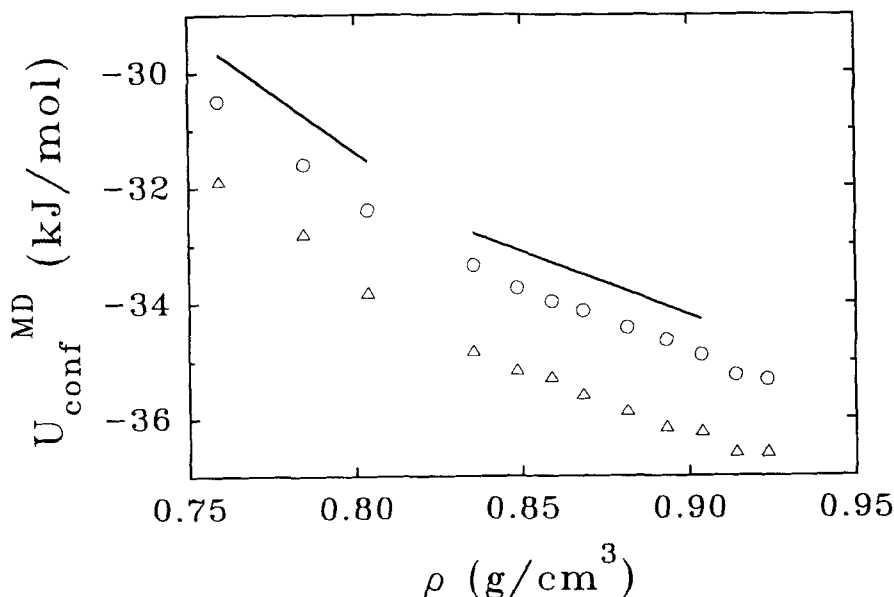
Figure 3 Density dependence of the configurational energy for pure cyclohexane (solid lines) and cyclohexane in the large cavity (circles) and in the small cavity (triangles).

The configurational energy as a function of density is presented in figure 3. Confinement of cyclohexane in the silica cavity leads to an increase of pressure and to a decrease of the energies. These changes are the result of cyclohexane-silica interactions. Density dependencies of pressure and the energies are almost the same as for bulk cyclohexane. In the small pore a larger fraction of molecules interacts directly with the silica surface what introduces an additional increase of the pressure and a decrease in the total and configurational energies, compare figures 2 and 3.

Structural properties

Examples of the centre-of-mass radial distribution function for pure cyclohexane are presented in figure 4. Up to the density, which corresponds to the experimental pressure of 0.6 kbar, the radial distribution functions show features typical for the liquid state. For higher densities they show fcc structure. These results are in good agreement with experimental studies of Wisotzki and Würflinger [2] who observed a phase transition between 0.6 kbar and 0.7 kbar.

From the positions of the mass centres we calculated the density of C_6H_{12} molecules, $g_c(r)$, as a function of the distance from centre of the silica cluster. Figure 5 shows the densities $g_c(r)$ for the large cavity. One observes about 5 Å thick layer near the silica surface. At higher densities the distribution function $g_c(r)$ shows succeeding layers that are not observed at low densities. We traced the positions of molecules during the simulation and we divided the molecules into "surface" molecules which were localised near the silica surface and "centre"
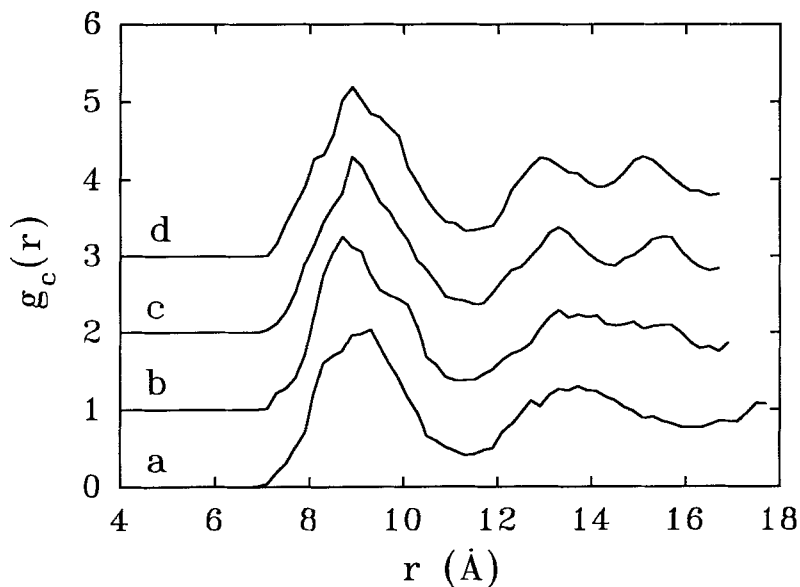
Figure 4 Centre-of-mass radial distribution functions of pure cyclohexane for densities: a – 0.7591 g/cm^3, b – 0.8036 g/cm^3, c – 0.8354 g/cm^3 and d – 0.9037 g/cm^3. The short vertical lines denote co-ordination zones for an ideal fcc lattice.

Figure 5 Density of C_6H_{12} as a function of distance, r, from the centre of the silica cluster for the large cavity, $D_c \cong 50$ Å, for densities: a – 0.7591 g/cm^3, b – 0.8930 g/cm^3, c – 0.9037 g/cm^3 and d – 0.9234 g/cm^3.

Figure 6 Centre-of-mass radial distribution functions of the centre molecules in the large cavity. The cyclohexane densities are the same as in figure 4. The short vertical lines denote co-ordination zones for an ideal fcc lattice.
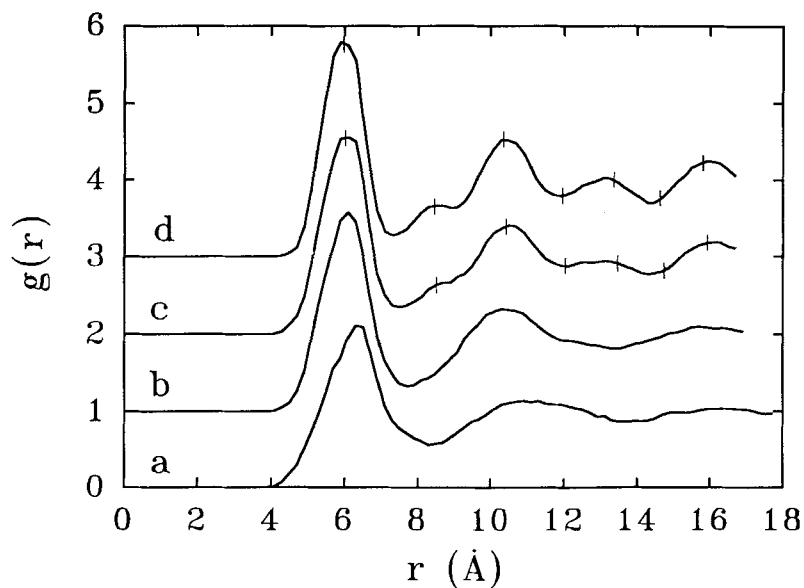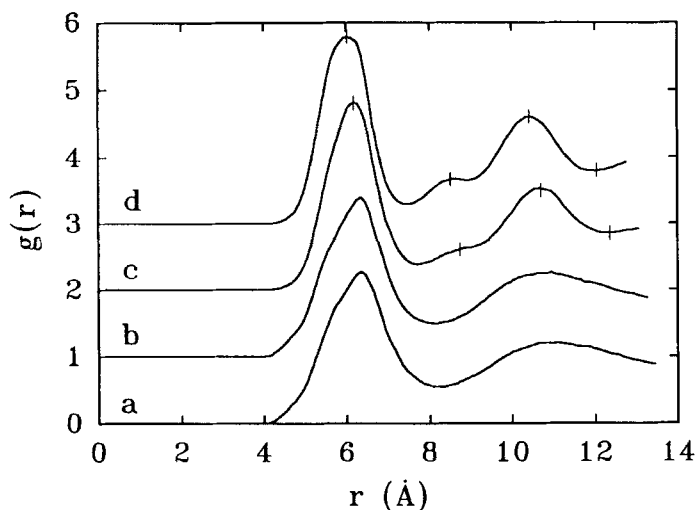
molecules which moved inside the inner part of the cavity. For the three lowest densities a few molecules exchanged their positions between the contact layer and inner part of the cavity, and those molecules were not counted either as the surface nor as the centre molecules.

Centre-of-mass radial distribution functions, $g(r)$, were calculated for centre molecules and for the large system ($D_c \cong 50$ Å) they are presented in figure 6. The fcc structure is observed for higher densities than in the case of bulk cyclohexane. For small cavity ($D_c \cong 30$ Å) the shapes of the radial distribution function are characteristic for the liquid state for the whole density range under consideration, and we do not present them here.

Dynamic properties

Positions, orientations and velocities of molecules recorded during the simulations were used to calculate time dependent correlation functions. The mean square displacement

$$\Delta r^2(t) = \frac{1}{3}\left\langle |\mathbf{r}_i(t) - \mathbf{r}_i(0)|^2 \right\rangle \tag{2}$$

was calculated for translational motion. For rotations we calculated the correlation function $G_{20}(t)$ which describes reorientations of the anisotropic part of Raman tensor for A_{1g} mode of C_6H_{12} [19]

$$G_{20}(t) = \left\langle P_2[\mathbf{u}_i(t) \cdot \mathbf{u}_i(0)] \right\rangle \tag{3}$$

and the angular velocity correlation functions for the spinning ($x = s$) and tumbling ($x = t$) motions

$$G_\omega^x(t) = \frac{\langle \omega_i^x(0)\omega_i^x(0)\rangle}{\langle \omega_i^x(t)\omega_i^x(0)\rangle} \tag{4}$$

In the above equations the angular brackets mean average values and P_2 is the Legendre polynomial of second rank. r_i is the position, u_i and ω_i^s are the the unit vector and angular velocity component parallel to the C_3 axis of the ith molecule and ω_i^t is the component of the angular velocity perpendicular to the C_3 axis. In analysis of molecular dynamics in the cavity the correlation functions were determined independently for the surface and centre molecules. The shapes of the correlation functions are very similar to those presented previously [4, 5]. Therefore, we limit the following discussion to the diffusion coefficient and rotational and angular velocity correlation times.

Table 3 Diffusion coefficients for centre, D^c, and surface, D^s, cyclohexane molecules.

ρ (g/cm^3)	D^c (10^{-9} m^2/s)	D^s (10^{-9} m^2/s)
Bulk		
0.7591	2.125	–
0.7846	1.616	–
0.8036	1.207	–
0.8354	$<3\cdot10^{-3}$	–
0.8484	$<3\cdot10^{-3}$	–
0.8588	$<3\cdot10^{-3}$	–
0.8680	$<3\cdot10^{-3}$	–
0.8812	$<3\cdot10^{-3}$	–
0.8930	$<3\cdot10^{-3}$	–
0.9037	$<3\cdot10^{-3}$	–
$D_c \cong 50$ Å		
0.7591	2.106	1.527
0.7846	1.491	1.203
0.8036	1.135	0.916
0.8354	0.673	0.468
0.8484	0.472	0.299
0.8588	0.425	0.293
0.8680	0.306	0.166
0.8812	0.276	0.145
0.8930	0.167	0.119
0.9037	$<6\cdot10^{-3}$	$<6\cdot10^{-3}$
0.9140[a]	$<6\cdot10^{-3}$	$<6\cdot10^{-3}$
0.9234[a]	$<6\cdot10^{-3}$	$<6\cdot10^{-3}$
0.7591	2.019	1.484
0.7846	1.502	1.206
0.8036	1.085	0.859
0.8354	0.583	0.415
0.8484	0.453	0.320
0.8588	0.422	0.294
0.8680	0.372	0.204
0.8812	0.257	0.166
0.8930	0.190	0.148
0.9037	0.156	0.120
0.9140[a]	0.153	0.104
0.9234[a]	0.122	0.081

[a] The densities extrapolated from data of Reference [2]

Diffusion coefficients listed in table 3 were obtained from the slopes of the mean square displacements [12]

$$D = \frac{1}{2} \frac{\Delta r^2(t_f) - \Delta r^2(t_i)}{t_f - t_i} \tag{5}$$

The calculations were carried out for time ranging from $t_i = 10\,ps$ to $t_f = 30\,ps$ where linear changes of $\Delta r^2(t)$ were observed. The maximum error of the diffusion coefficient obtained from the linear regression was $2 \cdot 10^{-12}\,m^2/s$ for pure cyclohexane and $4 \cdot 10^{-12}\,m^2/s$ for cyclohexane in the cavities. To calculate rotational relaxation times, τ_{20}, the correlation functions $G_{20}(t)$ were integrated up to 30 ps. The correlation times of angular velocities for the spinning and tumbling motions, τ_ω^s and τ_ω^t, were obtained by integration of the corresponding correlation functions up to 5 ps. To estimate statistical uncertainty in the correlation times the formulas worked out by Zwanzig and Ailawadi [20] and Frenkel [21] were used. The maximum errors of the rotational relaxation time were 7.8% and 6.1% for the surface and centre molecules in the small cavity at the highest density. In the case of the angular velocity correlation time the maximum errors were detected in pure cyclohexane for the lowest density and they were 1.6% for the spinning motion and 1% for the tumbling one.

Changes of the diffusion coefficient, rotational and angular velocity correlation times with density for the bulk system and for the centre and surface molecules in the large cavity, $D_c \cong 50\,\text{Å}$, are presented in figures 7–9.
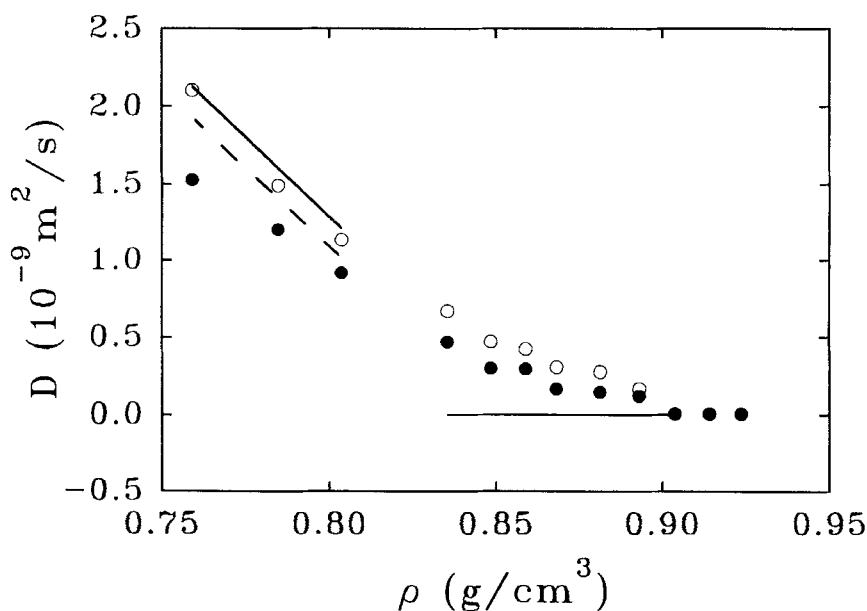
Figure 7   Diffusion coefficients as a function of density for pure cyclohexane (solid lines), centre (open circles), and surface molecules (full circles) in the large cavity, $D_c \cong 50\,\text{Å}$. The broken line represents experimental diffusion coefficients in pure liquid [22].

Figure 8   Rotational relaxation times as a function of density. Symbols as in figure 6.

Figure 9   Density dependence of the angular velocity correlation times for spinning, τ_ω^s, and tumbling motions, τ_ω^t. Symbols as in figure 6.

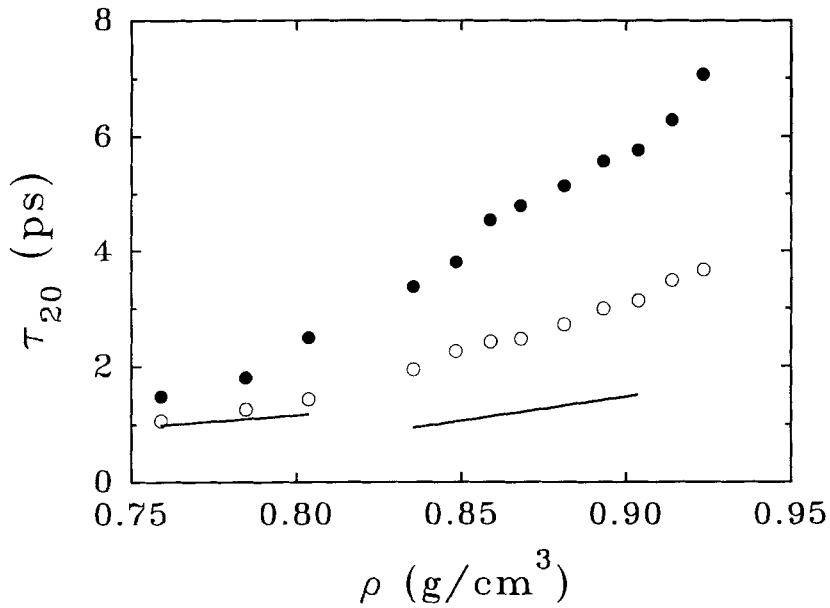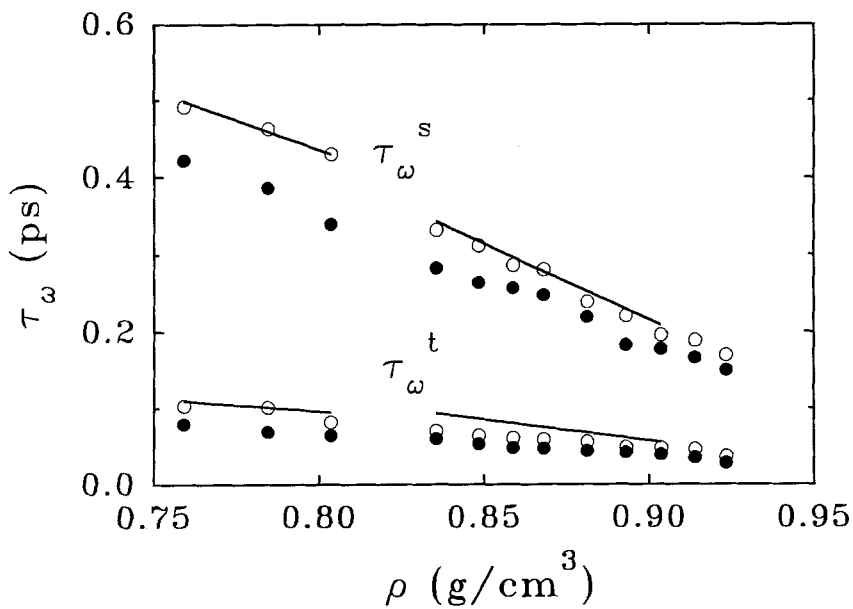For bulk cyclohexane a sharp drop of the diffusion coefficient indicates the liquid-plastic phase transition for a pressure value somewhere between 0.6 and 0.7 kbar [2]. The diffusion coefficients in the liquid state are slightly larger than the experimental values obtained by Jonas *et al.* [22]. The observed discrepancies may result from the rigid approximation and the simplified structure of the cyclohexane molecule. One has to note that these two factors affect molecular motion in a contrary manner. The rigidity of the molecules produces additional restrictions of molecular motion, whereas the united-atom approximation reduces them. Molecules in the cavity of 50 Å diameter behave like a liquid up to density corresponding to the experimental pressure of 2.5 kbar and just above this density their translational motion is frozen. For the small cavity, $D_c \cong 30$ Å, even at the highest density a small diffusion of molecules is still observed. These results correspond nicely to the pair radial distribution functions presented in the previous section, compare figures 4 and 6. Figure 7 shows that mobility of the surface molecules is lower than that of the centre molecules. The observed differences result from different neighbourhoods of the surface and centre molecules. A centre molecule interacts directly with moving cyclohexane molecules, whereas forces acting on a surface molecule originate also from rigid silica surface.

The relaxation time τ_{20} describes reorientations of C_3 axis of cyclohexane, and it is related to the angular velocity correlation time for tumbling motion, τ_ω^t. In bulk cyclohexane both τ_{20} and τ_ω^t shown small changes with density. However, across the liquid-plastic phase transition point one observes clear decrease in the reorientational time τ_{20}, compare figure 8, and small increase in the correlation time τ_ω^t, see table 4 and figure 9. This observation suggests that the density jump makes the tumbling motion slightly less restricted in the solid phase. Such effect had been observed near the melting point [4]. In the liquid state collisions between molecules, which result from translational motion, contribute to hindrances in the tumbling motion, whereas in the plastic phase this contribution decreases due to the ordered and frozen positions of molecules. This conclusion is confirmed by the behaviour of molecules in the cavities for which an increase of density increases the relaxation time τ_{20} and decreases the time τ_ω^t, see figures 8 and 9. In this case, the cyclohexane molecules are still in the liquid state. Higher density combined with relative large mobility of molecules lead to greater hindrances of the tumbling motion. For molecules in the cavity additional restrictions are result of interactions with silica. It is clearly visible in figure 8 that shows much slower relaxation of the centre molecules. Rotations of the surface molecules are independent of the cavity size, compare table 4, as interactions of molecules from the first layer with the silica surface and with neighbouring molecules do not depend on the cavity diameter. A centre molecule feels the silica surface through the surface and other centre molecules, and its motion is perturbed by surface interactions to a different degree depending on the distance from the surface. Because the number of the centre molecules which are not influenced at all or influenced only slightly by the silica surface increases with cavity diameter, one observes diminishing of the relaxation time τ_{20}^c with cavity size.

Figure 9 shows that the freedom of the spinning motion is much greater than that of the tumbling motion. Confinement of the molecules in silica cavity does not change the density dependence of the angular velocity correlation time for the spinning motion, τ_ω^s. For the centre molecules the values of the time τ_ω^s are almost the same as for pure cyclohexane. Smaller values for the surface molecules

Table 4 Rotational correlation times τ_{20}^{c} and τ_{20}^{s}, and relaxation times of angular velocity, τ_{ω}^{xc} and τ_{ω}^{xs} ($x = s$ for the spinning and $x = t$ for the tumbling motion), for the centre and surface molecules.

ρ (g/cm³)	τ_{20}^{c} (ps)	τ_{20}^{s} (ps)	$\tau_{(i)}^{sc}$ (ps)	$\tau_{(i)}^{ss}$ (ps)	$\tau_{(i)}^{tc}$ (ps)	$\tau_{(i)}^{ls}$ (ps)
Bulk						
0.7591	1.00	–	0.501	–	0.111	–
0.7846	1.09	–	0.454	–	0.097	–
0.8036	1.18	–	0.433	–	0.091	–
0.8354	0.97	–	0.338	–	0.095	–
0.8484	1.06	–	0.322	–	0.086	–
0.8588	1.13	–	0.303	–	0.082	–
0.8680	1.18	–	0.273	–	0.070	–
0.8812	1.30	–	0.248	–	0.067	–
0.8930	1.41	–	0.241	–	0.062	–
0.9037	1.56	–	0.202	–	0.057	–
0.7591	1.06	1.49	0.492	0.422	0.103	0.079
0.7846	1.26	1.81	0.463	0.386	0.101	0.069
0.8036	1.44	2.50	0.430	0.339	0.082	0.064
0.8354	1.94	3.37	0.332	0.283	0.070	0.060
0.8484	2.26	3.80	0.312	0.264	0.064	0.053
0.8588	2.43	4.53	0.287	0.257	0.061	0.048
0.8680	2.48	4.78	0.281	0.248	0.059	0.047
0.8812	2.73	5.13	0.239	0.219	0.056	0.044
0.8930	3.00	5.57	0.221	0.183	0.049	0.042
0.9037	3.13	5.76	0.196	0.178	0.048	0.039
0.9140[a]	3.48	6.29	0.189	0.166	0.046	0.035
0.9234[a]	3.67	7.07	0.170	0.150	0.037	0.028
$D_c \cong 30$ Å						
0.7591	1.03	1.68	0.483	0.406	0.095	0.074
0.7846	1.27	1.82	0.448	0.373	0.087	0.069
0.8036	1.69	2.56	0.421	0.346	0.078	0.067
0.8354	2.25	3.26	0.342	0.289	0.065	0.054
0.8484	2.56	3.70	0.306	0.278	0.058	0.044
0.8588	2.91	4.33	0.298	0.249	0.053	0.043
0.8680	3.03	4.49	0.281	0.237	0.051	0.042
0.8812	3.53	5.31	0.271	0.209	0.045	0.037
0.8930	3.83	5.85	0.210	0.198	0.045	0.033
0.9037	4.22	5.97	0.207	0.183	0.042	0.031
0.9140[a]	4.86	6.60	0.185	0.155	0.040	0.027
0.9234[a]	5.22	7.39	0.167	0.143	0.033	0.022

[a] The densities extrapolated from data of Reference [2]

indicate restrictions in the spinning motion originated from the interactions with silica. Similarly as in our previous study, the times τ_{ω}^{s} do not change with the cavity diameter what suggests that the immediate neighbourhood is essential for hindrances of the spinning motion.

CONCLUSIONS

MD simulation of pure cyclohexane properly predicts the liquid-plastic phase transition. In the plastic phase, for densities corresponding to the experimental

pressure 0.7 kbar and higher molecular translations are frozen but rotational freedom of molecules is still observed. A transition to the solid state makes the spinning motion more difficult, whereas the tumbling motion becomes slightly less restricted.

Confinement of molecules in the cavity shifts the transition point towards higher densities. For a large cavity, $D_c \cong 50$ Å, the transition point was found for densities corresponding to experimental pressures between 2.5 kbar and 3 kbar. In the case of the small cavity, $D_c \cong 30$ Å, for the density range under consideration, a transition to the plastic phase was not observed. One may suspect that for the small cavity the surface interactions greatly affect the dynamics of most molecules and prevent a transition to the solid phase. Except for the silica surface, the cavity model used in this work is very regular which suggest that forces originated from silica surface play crucial role in dynamics of molecules in pores. However, the geometrical restrictions such as pore shape and interconnectivity of pores in real sol-gel glass may additionally affect behaviour of molecules.

Acknowledgements

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