RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 46, NUMBER 1 1 JULY 1992-I

Rapid Communications

Rapid Communications are intended for the accelerated publication of important new results and are therefore given priority treatment both in the editorial office and in production. A Rapid Communication in **Physical Review B** *should be no longer than 4 printed pages and must be accompanied by an abstract. Page proofs are sent to authors.*

Geometrically restricted ultrathin (20-nm) film of cyclohexane: A metastable phase

R. Mu and V. M. Malhotra
Department of Physics and Molecular Science Program, Southern Illinois University at Carbondale, Carbondale, Illinois 62901-4401

(Received 15 October 1991; revised manuscript received 13 April 1992)

We present experimental evidence that when the dimensions of cyclohexane films are finite a new metastable phase is manifested. This was ascertained from comparative infrared measurements at $90 < T < 300$ K on three different-sized films of cyclohexane, i.e., 20 nm, 126 nm, and 12 μm, geometrically restricted in ZnSe cylinders.

It is recognized that the thermodynamic and dynamic properties of fluids are considerably altered, relative to their bulk, when the fluids are physically restricted in porous materials with radii < 30 nm.[1-5] Undoubtedly, with the surface-to-volume ratio of the confined fluids being very large, the surface structure of the confining medium will play an important role in governing the aforementioned properties of the confined fluid. This should be especially true if there is a strong interaction between the confined fluid and the confining material's surface. Almost all the work reported on porous materials has been on porous silica glasses.[1-5] Few attempts[2,5] though have been made to coat the porous silica glasses with organic derivatives to mitigate surface-fluid interactions or to enhance the wettability of the surface. At present, what role the surfaces and the shapes of the confining medium play in altering the thermodynamic properties of finite-size systems is yet to be ascertained.

In this paper, we report the thermodynamic behavior of an ultrathin film of cyclohexane which was geometrically confined in a ZnSe cylinder. From comparative vibrational measurements at $90 < T < 300$ K on finite (20-nm), semifinite (126-nm), and infinite (12-μm) films of cyclohexane, it is shown, consistent with the theoretical predictions of Sanchez, Mejia-Lira, and Moran-Lopez,[6] that on limiting the physical size of the sample a metastable state is produced.

It is well known[4,7] that cyclohexane has two stable solid phases at $T < 280$ K. Cyclohexane crystallizes into the fcc (S_C) phase at 280 K. The S_C phase, though plastic in nature, is stable at $186 < T < 280$ K. At 186 K the cyclohexane undergoes a structural order-disorder transition. Below 186 K the symmetry of the stable lattice phase is monoclinic (S_M). Burns and Dacol[8] suggest that in the plastic phase "the individual molecules are in one of several orientational positions with a small energy barrier between the positions." Therefore, when the S_C phase of cyclohexane is quenched (at 77 K), the "plastic crystal glass" is formed.[8] The cyclohexane molecules, in the plastic crystal glass phase, are in a frozen-in rotational disorder. On annealing the glass phase at 149 K, it rapidly converts into the equilibrium S_M phase. On the other hand, Zhizhin *et al.*[9] reported, using their infrared measurements, that the S_M and S_C phases coexist at around cubic-to-monoclinic transition temperature and the "hybrid mixture" of phases disappears within 1 K.

Since we were interested in understanding the effects of geometrical confinement and the surfaces other than porous silica, we fabricated, using the photolithographic technique, ultrathin chromium O rings on ZnSe optical flats. The thickness of the O rings was monitored with a quartz crystal, and the maximum error in thickness of the O ring was $< 10\%$. The details of the fabrication of the O rings, along with the temperature-dependent infrared sample cell design, will be reported elsewhere.[10] The optical flats were thoroughly cleaned,[4] and the cyclohexane sample was confined between two ZnSe optical flats. To elucidate the effects of finite thickness on the thermodynamic properties of cyclohexane, we made comparative temperature-dependent infrared measurements on finite-, semifinite-, and infinite-sized films. The high-resolution infrared data were collected in both heating and cooling modes. The sample temperature was raised or lowered at a rate of 0.1 K/min. The samples were held at the desired temperature for 25 min before 100 interferograms at 0.25 cm^{-1} resolution were collected. A fast-scanning Nicolet 740 Fourier-transform infrared spectrometer was used to collect the data. Other relevant recording conditions are mentioned elsewhere.[11]

From a detailed, comparative analysis of the observed infrared spectra of finite film, semifinite film, and infinite film of cyclohexane at $90 < T < 310$ K (in both heating and cooling modes), we can summarize our results as follows: (a) Irrespective of the thickness of the cyclohexane film, the cyclohexane froze at 280 ± 1 K and crystallized into an expected S_C phase. Also, within the experimental temperature uncertainty, i.e., ±1 K, the cyclohexane melted at 280 K for all three films. Therefore, no hysteresis was observed for the melting-freezing transition of cyclohexane for finite, semifinite, and infinite thick films. (b) The infrared spectra at $190 < T < 280$ K for all three sized films were identical to those reported for bulk cyclohexane in the S_C phase.[8,9,12] (c) As expected, the semi-finite and infinite thick cyclohexane films transformed into the S_M phase at 186 ± 1 K. The order-disorder cubic-to-monoclinic transition reflected no hysteresis for semifinite and infinite films. (d) Unlike semifinite and infinite films, when finite-sized cyclohexane film was cooled, it abruptly transformed at 186 ± 1 K into a solid phase which is different from the expected S_M phase. The new solid (S_N) phase was stable at $180 < T < 188$ K. On further cooling of the finite-sized film, the S_N phase abruptly transformed into the S_M phase at 180 ± 1 K. Figures 1 and 2 depict the comparative infrared spectra, in two different vibrational regions, near the S_C-to-S_M transition for finite-sized and semifinite-sized cyclohexane films. As can be clearly seen from these figures, the S_N phase only appears for finite-sized film. (e) On heating the finite-sized cyclohexane film from the lowest temperature attained, i.e., 98 K, the monoclinic phase directly transformed into the S_C phase at 188 ± 1 K. The hysteretic behavior of finite-sized film for cubic-to-monoclinic transition is shown in Fig. 3. In view of the data presented in Figs. 1–3, we classify the S_N phase as a metastable phase of cyclohexane. It is worthwhile to emphasize here that the metastable phase was observed only for finite-sized cyclohexane film, even though our experimental conditions and the cyclohexane sample used were identical for all three sized films. (f) On annealing the metastable phase (at 186, 184, and 182 K for 2 h at each temperature) the infrared spectra were not affected. In view of this observation, along with the fact that our samples were cooled at a rate of 0.1 K/min, we discount that the S_N phase is the plastic crystalline glass phase. (g) Table I presents the observed vibrational modes in the four phases of the finite-sized film of cyclohexane, i.e., the liquid phase, the cubic phase, the metastable phase, and the monoclinic phase. Based on the data listed in Table I, we argue that the S_N phase is not a hybrid mixture of phases S_C and S_M as suggested by Zhizhin *et al.*[9] nor is it a high-pressure phase of cyclohexane as reported by Haines and Gilson.[12] It may be asserted that the vibrational modes observed in the S_N phase may in fact be a combination of modes from the S_M or S_C phase and the surface modes from the cyclohexane adsorbed on the ZnSe surface. However, we discount this possibility because of the following: (i) The interaction between nonpolar cyclohexane molecules and ZnSe surface is expected to be weak. Thus, no distinct surface

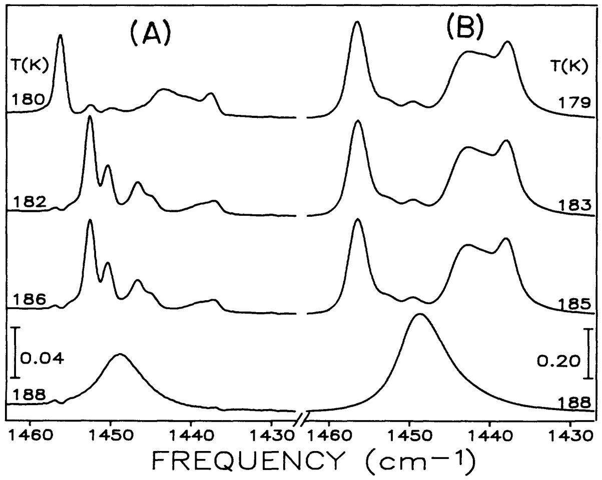

FIG. 1. The infrared spectra of (A) 20-nm and (B) 126-nm films of cyclohexane, in the C-H bending region, near the cubic-to-monoclinic phase transition. For this figure, data were collected in the cooling mode.

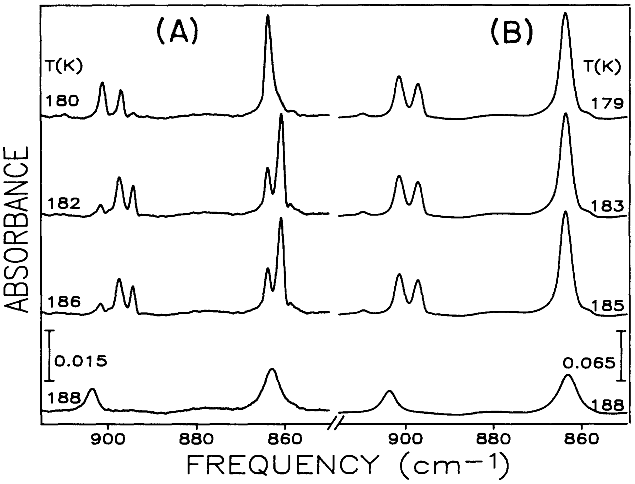

FIG. 2. The infrared spectra of (A) 20-nm and (B) 126-nm films of cyclohexane clearly showing the observance of the metastable phase for the 20-nm film. The spectra were collected in the cooling mode.

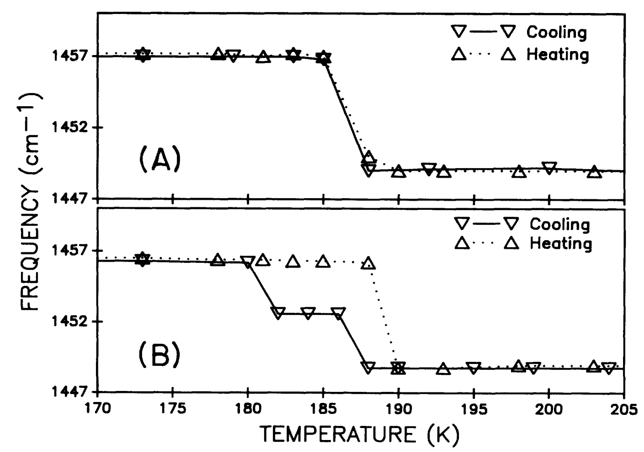

FIG. 3. (A) Spectra showing that no metastable phase is produced for the 126-nm film under identical experimental conditions. (B) The hysteretic behavior of the 20-nm film of cyclohexane depicting the presence of the metastable phase near the cubic-to-monoclinic transition.

TABLE I. Observed infrared frequencies (absorbance) of ultrathin (20-nm) cyclohexane film.

Liquid		Cubic		Metastable phase		Monoclinic		
(cm^{-1})	(abs.)	(cm^{-1})	(abs.)	(cm^{-1})	(abs.)	(cm^{-1})	(abs.)	Assignments
2927.6	(0.210)	2927.7	(0.229)	2925.7	(0.483)	2927.6	(0.364)	$\nu_{25}(E_u)$, $\nu_{12}(A_{2u})$
		2922.4	(0.222)	2921.6	(0.296)	2922.3	(0.259)	
				2910.6	(0.070)			
2910.9	(0.075)	2908.4	(0.083)	2908.1	(0.066)	2908.9	(0.085)	
2902.4	(0.045)	2900.8	(0.057)	2898.2	(0.035)	2897.7	(0.032)	
						2892.1	(0.010)	
2872.3	(0.014)	2868.8	(0.016)	2861.9	(0.028)	2863.8	(0.028)	$\nu_{26}(E_u)$, $\nu_{13}(A_{2u})$
2852.4	(0.109)	2850.0	(0.165)	2851.0	(0.146)	2849.9	(0.206)	
						1456.3	(0.065)	$\nu_{27}(E_u)$, $\nu_{14}(A_{2u})$
				1452.6	(0.072)	1452.8	(0.003)	
1450.2	(0.031)	1448.8	(0.040)	1450.4	(0.035)	1449.4	(0.003)	
				1446.7	(0.023)			
				1444.9	(0.013)	1443.7	(0.018)	
				1438.9	(0.008)	1439.8	(0.019)	
				1437.1	(0.010)	1437.0	(0.021)	
						1352.7	(0.006)	$\nu_{28}(E_u)$, $\nu_7(A_{1u})$
		1351.4	(0.003)	1351.3	(0.008)			
				1350.7	(0.011)			
				1350.2	(0.010)	1349.6	(0.010)	
						1342.2	(0.003)	
1255.5	(0.003)	1256.2	(0.004)	1254.3	(0.005)	1254.1	(0.009)	$\nu_{29}(E_u)$, $\nu_8(A_{1u})$
				1251.8	(0.008)	1252.0	(0.006)	
						1250.0	(0.009)	
						1106.0	(0.007)	$\nu_9(A_{1u})$
						1091.0	(0.001)	
		1039.9	(· · ·)	1040.5	(0.003)	1041.0	(0.005)	$\nu_5+\nu_{32}(E_u)$
				1016.3	(· · ·)	1018.7	(0.004)	
						909.6	(0.002)	$\nu_{30}(E_u)$
903.5	(0.007)	903.5	(0.009)	901.7	(0.004)	901.1	(0.016)	
				897.3	(0.014)	896.7	(0.010)	
				894.3	(0.011)			
861.5	(0.006)	862.9	(0.015)	864.0	(0.017)	863.8	(0.040)	$\nu_{31}(E_u)$
				860.8	(0.037)			

modes of adsorbed cyclohexane are expected.[13] (ii) Moreover, in our finite-sized film, there are approximately 46 layers of cyclohexane along the thickness of the film. If one adapted the hard-sphere approach, then there are 1.2×10^{12} molecules of cyclohexane on each surface of ZnSe. This implies that there are 5.28×10^{13} cyclohexane molecules in either the S_M or S_C phase. Therefore, the intensity of the S_M or S_C phase vibrational modes is expected to be 22 times larger than the surface vibrational modes at $180 \leq T \leq 186$ K. A careful examination of absorbances reported in Table I and of the observed behavior of vibrations presented in Figs. 1 and 2 clearly suggests that our results do not conform with the inclination that our observed S_N phase vibrations are in fact a combination of surface modes and vibrations from the S_M or S_C phase.

According to the geometrical shape of our cyclohexane samples, it can be argued that for finite-sized film the cyclohexane sample is bounded by a length scale L (thickness) in one direction but infinite in the others (radius of the O ring is 0.9 cm). Under the condition that the sample is bounded and has finite L, the phase transition temperature[6,14] is expected to scale with L, i.e.,

$$\Delta T = T_B - T_L \propto 1/L \,. \tag{1}$$

In Eq. (1), T_B and T_L are the bulk sample's transition temperature and the bounded sample's transition temperature, respectively. As pointed out earlier, for melting or freezing transition of finite-, semifinite-, and infinite-sized cyclohexane film, $\Delta T = 0$. For our finite-sized film, there are ~46 layers of cyclohexane molecules along scale L. It is possible the condition[14] for the depression in transition temperature, i.e., $l = L/L_0 \leq 1$ (where L_0 is the critical length for the depression to occur), is not met by our finite-sized film. If this is the case, then the S_C-to-S_M transition temperature is also not expected to be depressed.[4] In view of this, the observance of a metastable phase only for the finite-sized cyclohexane film seems very surprising.

Bulk cyclohexane has considerable rotational and reorientational motion in its cubic phase. However, Mu and

Malhotra,[4] from their recent specific-heat measurements, observed that for physically confined cyclohexane there are idle and nonidle molecules. The idle molecules are close to or at the surface of the confining silica medium. Unlike the silica surface, the major interaction between the ZnSe surface and cyclohexane is expected to be a van der Waals interaction. The consequence of this interaction could result in a hindered rotational motion of the cyclohexane molecules near both sides of the finite-sized film. Therefore, it is reasonable to expect that the "barrel-shaped" cyclohexane molecules are adsorbed on, with their triad axis perpendicular to, the ZnSe surface. At high temperatures, i.e., $T > 186$ K, there may be one to two idle layers of cyclohexane. However, as the sample is cooled and T approaches 186 K, the ordered (relative to the cyclohexane molecules in the interior of the film) surface region begins to grow. Thus, in our finite-sized film, near 186 K, two distinct regions can be visualized, i.e., one near the two surfaces where barrel-like cyclohexane molecules are stacked and one at the center of the film that is richer in molecules with considerable rotation motion. As discussed earlier, the interaction between the nonpolar cyclohexane molecules and ZnSe surface is weak, thus, no separate vibrational modes are expected from the stacked cyclohexane molecules.[13] Since for our finite-sized film $\Delta T = 0$, it is reasonable to think that the surface transition temperature (T_S) undergoes an ordinary transition, i.e., $T_S = T_B$.[6] Therefore, T_L should approach the lower S_M-S_C phase boundary of the equilibrium phase diagram of the infinite system. For our finite-sized film, the surface-to-volume ratio is relatively large. Therefore, perhaps the concentration of the ordered layers near the two surfaces of the film tends to stabilize the S_N phase. Trew, Pawley, and Smith,[15] from their molecular dynamics analysis of 128 molecules cyclohexane cluster, predict a rhombohedral phase for cyclohexane when the surface-to-volume ratio of cluster is large. It is possible that our metastable phase, in fact, has rhombohedral symmetry. Unfortunately, it is not feasible for us to suggest the symmetry of the S_N phase from infrared measurements alone. However, it is worth pointing out that Sanchez, Mejia-Lira, and Moran-Lopez[6] do suggest the possibility of the metastable phase when L is finite.

In summary, from our comparative experimental infrared measurements at $90 < T < 310$ K on cyclohexane physically restricted in ZnSe cylinders with $L = 20$ nm, 126 nm, and 12 μm, it is shown that a new metastable phase is produced when L is finite. We hope this paper will stimulate additional theoretical and experimental work to ascertain the formation of the metastable phase when the sample size is finite.

---

[1] D. D. Awschalom and J. Warnock, Phys. Rev. B **35**, 6779 (1987); M. B. Ritter, D. D. Awschalom, and M. W. Shafer, Phys. Rev. Lett. **61**, 966 (1988).

[2] J. M. Drake and J. Klafter, Phys. Today **43** (5), 46 (1990).

[3] R. H. Torii, H. J. Maris, and G. D. Seidel, Phys. Rev. B **41**, 7167 (1990).

[4] R. Mu and V. M. Malhotra, Phys. Rev. B **44**, 4296 (1991).

[5] C. L. Jackson and G. B. McKenna, J. Chem. Phys. **93**, 9002 (1990).

[6] J. M. Sanchez, F. Mejia-Lira, and J. L. Moran-Lopez, Phys. Rev. Lett. **57**, 360 (1986).

[7] R. Khan, R. Fourme, D. Andre, and R. Renaud, Acta. Crystallogr., Sect. B **29**, 131 (1973).

[8] G. Burns and F. H. Dacol, Solid State Commun. **51**, 773 (1984), and references therein.

[9] G. N. Zhizhin, E. L. Terpugov, M. A. Moskaleva, N. I. Bagdanskis, E. I. Balandov, and A. I. Vasil'ev, Fiz. Tverd. Tela (Leningrad) **14**, 3612 (1972) [Sov. Phys. Solid State **14**, 3028 (1973)].

[10] R. Mu, V. M. Malhotra, R. N. Zitter, T. M. Masden, and A. Chen (unpublished).

[11] V. M. Malhotra, S. Jasty, and R. Mu, Appl. Spectrosc. **43**, 638 (1989); S. Jasty, P. D. Robinson, and V. M. Malhotra, Phys. Rev. B **43**, 13215 (1991).

[12] J. Haines and D. F. R. Gilson, J. Phys. Chem. **93**, 7920 (1989).

[13] M. J. D. Low and B. K. Sahay, J. Colloid Interface Sci. **49**, 69 (1974).

[14] D. Sornette, Phys. Rev. B **31**, 4672 (1985).

[15] A. S. Trew, G. S. Pawley, and A. C. Smith, Acta Crystallogr., Sect. A **46**, 979 (1990).