

Role of end chains in the reentrant behavior of a nonpolar system

T. R. Bose,* D. Ghose,[†] C. D. Mukherjee,[‡] J. Saha, M. K. Roy, and M. Saha

Department of Physics, University College of Science, 92 Acharya Prafulla Chandra Road, Calcutta 700 009, India

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In this paper we propose to estimate the role of chain conformations in bringing about reentrant polymorphism in a nonpolar sample of mesogens. To this end we also show that the reentrant phenomenon is built in the McMillan model, if one explicitly incorporates the effect of tail-chain conformations in the molecular potential instead of treating the chains as an extension of the rigid part. The model is next utilized to predict the single reentrance $I-N-Sm-N_{re}$ with lowering of temperature in a nonpolar system.

I. INTRODUCTION

Since the discovery of reentrant polymorphism in a binary mixture of two polar compounds,¹ a large number of investigations have been carried out in this field. Liquid-crystalline systems exhibiting such reentrant polymorphism $I-N-Sm-N_{re}$ and the double (or triple) reentrant phase sequence consist of organic molecules usually with three or four aromatic rings with ester linkages and having polar cyano or nitro-end groups.²⁻⁹ Apart from pure compounds,^{3,4} such reentrant polymorphism with a lowering of temperature is also exhibited by binary mixtures of polar-polar,^{2,7,9} polar-nonpolar,¹⁰ or even by nonpolar-nonpolar compounds.^{11,12} The last one however only shows the single reentrant phase sequence. Further, as a given homologous series is ascended the reentrant phase sequence is shown by the higher homologs (e.g., usually by the octyloxy, nonyloxy, etc. members) which are neither very short nor very long. These findings indicate that the dipolar force plays a crucial role in the reentrant polymorphism. There are theoretical models¹³⁻²¹ that emphasize this role of dipolar force to bring about the phase sequence. A number of theories assume some sort of bimolecular organization (dimers)¹³⁻¹⁹ or even trimers or n -mers²⁰ with antiparallel association that compensates (not always fully) the dipole moments. This system of dimers or n -mers together with existing monomers can bring about the desired phase sequence. Such theories can also explain the variation of layer thickness¹⁶⁻¹⁸ as an interdigitation or reorientation¹⁸ (in the case of constant layer thickness) of the component systems in a mean-field approach. These theories essentially show that the high-temperature smectic phase is an induced phase and the reentrant nematic phase is brought about by a competition between two incommensurate lengths. This two-length theory is also one of the main ingredients of the Landau theory of the phase transition developed by Prost and Barois.^{22,23} A further review of theories and experiments for reentrant nematic phases can be found in Refs. 24 and 25.

However, the occurrence of single reentrance $I-N-Sm-N_{re}$ (Refs. 11 and 12) in a binary mixture of nonpolar compounds cannot possibly be due to such dipolar forces.

In fact, for such systems, observation¹² on layering thickness shows no hint for the kind of dimerization as is found in reentrant systems with polar compounds. The above result, together with the observation that in all the systems discussed the reentrant phase usually occurs for certain members (usually eighth or ninth) of the homologous series, indicate that the tail chains should have some active role in bringing about the reentrance. Dowell²⁶⁻²⁹ proposed a lattice model for condensed phases that predicted reentrance in a single-component nonpolar system. In that model, it is seen that a segregated packing of cores beside cores and chains beside chains occurs with a lowering of temperature leading to a usual smectic phase. With further lowering of temperature, the chains become less flexible, and packing differences between the rigid cores and tail chains decrease. Thus, the need for segregated packing of rigid cores with cores (and tail chains with tail chains) is overcome by entropy of unsegregated packing, leading to the disappearance of the smectic- A phase and the appearance of the reentrant nematic phase. In other words, the Dowell model holds the change in chain configuration responsible for reentrance. We present in this section some results we have obtained on the role of chains in bringing about reentrance in a single-component nonpolar sample. As in the case of polar systems,¹⁶⁻¹⁸ our present study is also based on a molecular mean-field approach and the starting point, so to say, is again the McMillan model.³⁰ Here, however, we show that the reentrant phenomenon is built in the McMillan model, if one explicitly incorporates the effect of tail-chain conformations in the molecular potential instead of treating the chains as an extension of the rigid part. The model is used next to predict the single reentrant phase sequence $I-N-Sm-N_{re}$ with lowering of temperature in an idealized nonpolar system. Our results also indicate that chain conformations alone can give rise to reentrance for certain intermediate members of a homologous series only under some very restrictive conditions.

II. THEORY

Let us consider a system of molecules, each with a rigid core (maybe consisting of three or four aromatic rings),

and chains on either side of it. We further imagine that the linkages are apolar. In order to bring forth the rationale behind our extension of the McMillan model we first review briefly the essential aspects of McMillan's work.³⁰

In his model, McMillan used a simple form of pair interaction potential suggested by Kobayashi

$$V_{12} = U(r) + W(r)P_2(\cos\theta_{12}), \quad (1a)$$

where r is the separation between the centers of mass of the molecules and θ_{12} is the angle between their long axes, $U(r)$ represents the short-range central force while the term with $W(r)$ describes the orientational forces due to the anisotropic dispersion forces, quadrupole-quadrupole forces, etc.³¹ McMillan further chose the following specific forms of $U(r)$ and $W(r)$:

$$\begin{aligned} W(r) &= -\frac{v}{nr_0^3\pi^{3/2}}\exp[-(r/r_0)^2], \\ U(r) &= \partial W(r), \end{aligned} \quad (1b)$$

where v and ∂ are constants characterizing the strengths of the two parts of interactions and r_0 , which specifies the range of interaction, is of the order of the length of the rigid part (core) of the molecule. The mean field (keeping only the lowest-order nonvanishing term of the Fourier expansion and consistent with the periodic structure in a smectic phase) described by the pair interaction potential is given by

$$\begin{aligned} V_M(\cos\theta, z) &= -v \left\{ \partial\alpha\tau \cos\left[\frac{2\pi z}{d}\right] \right. \\ &\quad \left. + \left[\eta + \alpha\sigma \cos\left[\frac{2\pi z}{d}\right] \right] P_2(\cos\theta) \right\}, \end{aligned}$$

where η is the orientational order parameter, $\eta = \langle P_2(\cos\theta) \rangle$; τ is the layering order parameter, $\tau = \langle \cos(2\pi z/d) \rangle$; σ is the layering cum orientational order parameter,

$$\sigma = \langle P_2(\cos\theta)\cos(2\pi z/d) \rangle,$$

and

$$\alpha = 2 \exp[-(\pi r_0/d)^2], \quad (1c)$$

d being the layer thickness.

Defining $\eta \neq 0, \tau = \sigma = 0$ as the nematic and $\eta \neq 0, \tau \neq 0, \sigma \neq 0$ as a smectic phase, a phase sequence Sm- N - I can be reproduced. Moreover, a phase diagram for a homologous series can also be obtained by varying α . As a homologous series is ascended, d (which is taken as equal to the molecular length as the smectic phase considered by McMillan was a smectic- A_1 phase) increases; r_0 remaining constant α likewise increases. In subsequent work of the authors³² it has been conclusively established that the phase sequence Sm- N - I can be obtained even when one ignores the short-range central force term in the Kobayashi potential [Eq. (1a)] and the phase diagram for a homologous series reproduced with this simplified potential hardly differs in any essential way

from the diagram with $U(r)$ taken into consideration.

It has also been shown by Lee *et al.*³³ that the monotonic rise of Sm- N and Sm- I temperatures in McMillan's model, which contradicts experimental results, can be rectified by modifying $W(r)$ as

$$W(r) = -\frac{v}{n_x n_y} \exp[-(r/r_0)^2], \quad (2)$$

where n_x and n_y are the number densities of molecules along x and y directions.

Thirdly, the flexibility of polymethylene chains was explicitly taken into consideration by Marcelja,³⁴ Mukherjee *et al.*,^{35,36} and by Luckhurst³⁷ to reproduce the even-odd effect in N - I and Sm- N transitions.

In the present paper we draw attention to another inadequacy of the McMillan model which can be rectified to give rise to the possibility of reentrant polymorphism, though in a very narrow range of model parameters.

In the McMillan model r_0 which is the range of pair interaction [Eq. (1b)] and also the layer thickness d in Eq. (1c) are constants (independent of temperature) for a member of a homologous series. We think this to be an oversimplification for flexible molecules. The layer thickness, which is taken to be the length of a molecule, should change with temperature as the average configuration of the end chains changes. Moreover, the contribution to the longitudinal polarization of a molecule from the C—C bonds of the tails would also change with temperature. As the temperature is lowered the all-*trans* contribution with maximum longitudinal polarizability will be favored. In other words the polarizability spreads out along the molecular axis as the all-*trans* configuration becomes more and more probable thereby changing the shape of the Gaussian pair potential. The range of interaction therefore gets changed. From the above consideration it is clear that a change in the value of r_0 and d with temperature may bring in a change in the value of the α parameter in contrast to being a constant in the McMillan model. Over and above this, in the McMillan model α is varied to take care of a homologous series. But there is no way of linking a specific value of α to a particular member. To do this we have to put specific values of d and r_0 for a member of a homologous series. As explained above these d and r_0 values can also vary with temperature. This change of d and r_0 (and the associated change in α) from member to member, and also their change with temperature for a particular member, is what we endeavor to introduce in this work.

The change in d from member to member and also with temperature is rather straightforward. This can be done,^{34,35} which will be discussed later in this section, by generating explicitly all possible conformations of chains following Flory. Further, as more and more of the C—C bonds are added, the polarizability of the molecules should spread out along the axis. The r_0 should, therefore, increase for higher members. Moreover, as the temperature is reduced the chains should straighten out more resulting in a rise in the value of net polarizability of the molecules. The maximum spread occurs when the chains are in an all-*trans* conformation. We assume a "workable" though very simplified and intuitive variation of the

core length. In this model the width of the Gaussian r_c consists of two parts

$$r_c = r_{c0} + \Delta r$$

where r_{c0} is the length of the central rigid aromatic part of the molecule without any of the chain segments. This r_{c0} , which remains constant with temperature, is analogous to r_0 in McMillan's α . The Δr is the spread in the Gaussian due to the straightening of the chain part. If we, for the sake of simplicity, consider that the rigid part extends to the whole all-*trans* length at $T=0$ K we can take Δr at some other temperature to be the probable all-*trans* length, i.e., Δr is the all-*trans* length of the chains x all-*trans* probability (P_{tr}) at that temperature.

With these changes McMillan α is modified to

$$\alpha = 2 \exp \left[-\frac{\pi^2 (r_{c0} + \Delta r)^2}{\langle l \rangle^2} \right],$$

where $\langle l \rangle$ is the average length of the molecule to be calculated from the conformations of the molecule. The all-*trans* probability at any given temperature can also be calculated by generating all the conformations properly weighting them by the respective intrachain conformational energies. One further point is that in the application of the McMillan model to ordinary smectics it is observed that α calculated from T_{Sm-N} [using the expression (1c)] corresponds to the core length usually smaller than the geometrical size of the core, i.e., the core length relevant to α is a fraction K_c of r_c , the geometrical length. With this possibility α can be written in our model as

$$\alpha = 2 \exp \left[\frac{-\pi^2 K_c^2 (r_{c0} + \Delta r)^2}{\langle l \rangle^2} \right], \quad (3)$$

where K_c is taken as a constant for a given homologous series. Moreover, for a homologous series r_{c0} is a constant. Knowing r_{c0} and K_c , successive members can be treated individually with the addition of one C—C bond at one or either end. At this point we would like to point out an interesting aspect of α in Eq. (3). For a particular member of the homologous series McMillan's α of Eq. (1c) is a constant, independent of temperature. The α of the present model however changes with temperature. As the temperature changes, both Δr and $\langle l \rangle$ change and as a consequence α can, in certain cases, decrease [as evident from the results of Table III and Eq. (3)] with the lowering temperature giving rise to a reentrant nematic phase. Now, taking the pair interaction potential

$$W(r) = -\frac{V}{nr_c^3 \pi^{3/2}} \exp[-(r/r_c)^2] \quad (4)$$

[the alternative choice of the modified form of Eq. (2) is discussed later in this section] and following McMillan, we write the mean field experienced by a molecule

$$V_M = -v \left[\eta + \alpha \sigma \cos \frac{2\pi z}{d} \right] P_2(\cos \theta), \quad (5)$$

where the layer thickness d is equal to $\langle l \rangle$ as the smectic phase considered in this work is really a smectic- A_1 phase. The layer normal is taken as the z direction. v is the coupling constant characterizing the interaction strength and α is given by Eq. (3).

The order parameters are given by the self-consistent equations

$$\eta = \int \int P_2(\cos \theta) \exp(-V_M/kT) d(\cos \theta) (1/Z), \quad (6a)$$

$$\sigma = \int \int \cos \left[\frac{2\pi z}{d} \right] P_2(\cos \theta) \exp \times (-V_M/kT) d(\cos \theta) (1/Z), \quad (6b)$$

where Z is the partition function.

With this we write the free energy per particle in units of kT

$$F/kT = -\frac{1}{2}v(\eta^2 + \alpha\sigma^2) - \log_e Z$$

Calculation of $\langle l_c \rangle$ the average chain length and P_{tr} , the all-*trans* probability

To calculate P_{tr} and $\langle l_c \rangle$ we are to explicitly generate chain conformations using internal angles and the corresponding orientation in molecular frame. Adopting the convention of Flory³⁸ the transformation matrix from $(i+1)$ th frame attached to the $(i+1)$ th segment to the i th frame can be written as

$$T_i = \begin{pmatrix} \cos \delta & \sin \delta \cos \phi_i & \sin \delta \sin \phi_i \\ \sin \delta & -\cos \delta \cos \phi_i & -\cos \delta \sin \phi_i \\ 0 & \sin \phi_i & -\cos \phi_i \end{pmatrix},$$

where $\pi - \delta$ is the bond angle and ϕ_i dihedral angle for the i th chain segment.

In the rotational isomer model the dihedral angle can take three values. For a *trans* configuration the angle $\phi = 0^\circ$ and for the two gauche states (g^+, g^-) the values of ϕ are $+120^\circ$ and -120° , respectively. Therefore, a set of ϕ values for the segments gives a conformation of the chain. For a given conformation the components of the unit vector along the $(i+1)$ th C—C bond can be obtained in the rigid core frame by the following transformation:

$$\begin{pmatrix} u_{i+1} \\ v_{i+1} \\ w_{i+1} \end{pmatrix} = T_1 \cdots T_{i-1} T_i \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}.$$

The projection of the unit vector of the $(i+1)$ C—C bond along the molecular axis (defined as the axis of the rigid part of the molecule) is thus u_{i+1} . In units of C—C bond length, u_{i+1} is, in fact, the projected length of the bond along the molecular axis. Transforming all the C—C bonds and adding them we obtain the projected axial length of a chain for that conformation. The average of this projected length over all the conformations is taken to be $\langle l_c \rangle$. For the calculation of the average length, we need to weight the individual conformation in accor-

dance with the respective conformational energies. For a given conformation the conformation energy, i.e., the intermolecular interaction energy of a polymethylene chain of N segments,

$$u_{\text{int}} = \sum_{i=2}^N E(\xi_{i-1}, \xi_i),$$

where i indicates the chain segment number and ξ represents any of the three rotation isomer states t (*trans*), g^+ (*gauche*).

For polymethylene chains the rotation energies taken were

$$E(t, t) = E(g^+, t) = E(g^-, t) = 0,$$

$$E(t, g^+) = E(g^+, g^+) = 400 \text{ cal/mol},$$

$$E(g^+, g^-) = E(g^-, g^+) = 2000 \text{ cal/mol}.$$

The partition function Z_c for chain configuration is thus

$$Z_c = \sum_{\text{all conf.}} \exp(-U_{\text{int}}/kT).$$

As U_{int} of an all-*trans* state is zero, the all-*trans* probability P_{tr} is given by

$$P_{\text{tr}} = 1/Z_c,$$

$$\langle l_c \rangle = \frac{\sum_{\text{all conf.}} \sum_{i=1}^N U_i \exp(-U_{\text{int}}/kT)}{Z_c} = 2.0,$$

and $\langle l \rangle (=d) = r_{c0} + \langle l_c \rangle$.

The all-*trans* length for the N th homolog, assuming

chains on either side is

$$l_{\text{tr}} = \begin{cases} N(1 + \cos\delta), & N \text{ even} \\ (N+1) + (N-1)\cos\delta, & N \text{ odd} \end{cases}.$$

Now that we can calculate Δr and $\langle l_r \rangle$, we solve the set of self-consistent equations and the stable solution is picked up corresponding to the minimum of the free energy.

III. RESULTS AND DISCUSSION

Our model system consists of nonpolar molecules that have rigid cores with flexible chains on either side of them. We assume $\delta = 68^\circ$, typical of the polymethylene chain.³⁸ As discussed in Ref. 38, this value of the carbon-carbon bond angle is in accordance with the evidence provided by analysis of the x-ray diffraction of crystalline *n*-alkanes,^{39,40} by electron diffraction of gaseous *n*-alkanes from propane to heptane,⁴¹ and by the microwave spectrum of propane.⁴² Taking each chain segment to have unit length, calculation was done for different values of r_{c0} (in units of C—C bond length) for a homologous series with chain segment members up to $N=7$. We restricted ourselves to $N \leq 7$ primarily due to the excessive computation time needed for higher members. Taking T_{N-I} between 300 and 400 K the search for reentrance was continued down to a temperature about $\frac{1}{4}T_{N-I}$. This has been taken to be a typical range for mesophases of thermotropic liquid crystals. The lower bound is low enough for most systems to crystallize. Now, varying the input parameter α_{in} (value of α chosen at T_{N-I}) it is seen that reentrance can be obtained

TABLE I. Values of \mathcal{F} ($=T_{N-I}/T$) at transitions for the sixth homolog. (T_{N-I} has been taken to be 300 K and calculation was done up to $\mathcal{F}=3.8$; — indicating that the former phase prevails.)

α_{in}	$r_{c0}=1.7$			$r_{c0}=1.9$			$r_{c0}=2.0$		
	$I-N$	$N-Sm$	$Sm-N_{re}$	$I-N$	$N-Sm$	$Sm-N_{re}$	$I-N$	$N-Sm$	$Sm-N_{re}$
0.50	1.0	—	—	1.0	—	—	1.0	—	—
0.55	1.0	—	—	1.0	1.6	2.2	1.0	1.6	2.3
0.60	1.0	—	—	1.0	1.4	2.6	1.0	1.4	2.6
0.65	1.0	1.4	2.6	1.0	1.4	2.8	1.0	1.4	2.8
0.70	1.0	1.4	2.8	1.0	1.4	3.0	1.0	1.4	3.2
α_{in}	$r_{c0}=2.2$			$r_{c0}=2.6$			$r_{c0}=3.0$		
	$I-N$	$N-Sm$	$Sm-N_{re}$	$I-N$	$N-Sm$	$Sm-N_{re}$	$I-N$	$N-Sm$	$Sm-N_{re}$
0.50	1.0	—	—	1.0	1.8	2.4	1.0	1.8	2.6
0.55	1.0	1.6	2.4	1.0	1.6	2.8	1.0	1.6	3.2
0.60	1.0	1.4	2.8	1.0	1.4	3.2	1.0	1.4	3.4
0.65	1.0	1.4	3.0	1.0	1.4	3.4	1.0	1.4	3.8
0.70	1.0	1.4	3.2	1.0	1.2	3.8	1.0	1.2	—
α_{in}	$r_{c0}=3.4$			$r_{c0}=3.6$			$r_{c0}=3.8$		
	$I-N$	$N-Sm$	$Sm-N_{re}$	$I-N$	$N-Sm$	$Sm-N_{re}$	$I-N$	$N-Sm$	$Sm-N_{re}$
0.50	1.0	1.6	3.0	1.0	1.6	3.2	1.0	1.6	3.7
0.55	1.0	1.6	3.4	1.0	1.6	3.6	1.0	1.4	3.8
0.60	1.0	1.4	3.8	1.0	1.4	—	1.0	1.4	—
0.65	1.0	1.4	—	1.0	1.4	—	1.0	1.4	—
0.70	1.0	1.2	—	1.0	1.2	—	1.0	1.2	—

TABLE II. Phase sequence of other members when the fitted parameters of $N=6$ are extended to them. — indicates that the former phase prevails ($r_{c0}=2.0$, $T_{N-I}=300$ K, and $K_c=0.6405$).

No. of chain segments	\mathcal{F} at			Value of α at phase transitions		
	$I-N$	$N-Sm$	$Sm-N_{re}$	$I-N$	$N-Sm$	$Sm-N_{re}$
4	1.0	—	—	0.081		
5	1.0	—	—	0.344		
6	1.0	1.350	2.60	0.620	0.545	0.209
7	1.0	1.0	—	0.848	0.837	

for $N=4-7$ for $r_{c0} \lesssim 3.8$. For larger values of r_{c0} the competitive effects of Δr produced by all-*trans* probability and $\Delta \langle l \rangle$ have nearly equal and opposite effects on the layering interaction parameter α ; it either decreases very slowly, or even increases marginally with lowering of temperature such that the reentrance temperature becomes too low. Admissible values of α_{in} also lie in a narrow range between 0.4 and 0.8. Some results on $N=6$ are shown in Table I. The tabulated results clearly show that $T_{Sm-N_{re}}$ goes down with increasing r_{c0} . Therefore, what we may infer is that a reentrance is possible but at a small value of r_{c0} so that $T_{Sm_{re}}$ is not too low. A value of r_{c0} around 4 (i.e., length of the core is four times that of a C—C bond) is, however, too small for a real system where the core consists usually of more than one phenyl ring. Another aspect of our study is whether a reentrance occurring in a particular member persists over other members as well. It is to be pointed out that though we could reproduce reentrance for $N=4-7$, we had to use different r_{c0} and α_{in} for different members. What we ought to do is to fix a value of K_c from one

member showing reentrance and use the same value of K_c (and also r_{c0}) for other members as well. For example, we have chosen $N=6$ for finding K_c . Taking the $T_{N-I}=300$ K data for $\alpha_{in}=0.62$ we find $K_c=0.6405$. Using this K_c and taking $r_{c0}=2.0$ we can find the corresponding α_{in} for each member from $N=4-7$ and go on looking for the phase sequences for each member. Results are shown in Table II. It is seen that while we started with parameters appropriate for reentrance in $N=6$, we do not have this phenomenon repeated in other members. What happens is that the computed α_{in} for a lower member is quite low. For such systems all-*trans* probability p_{tr} at T_{N-I} is fairly high, but due to a limited number of conformations, P_{tr} is found to increase rather slowly at lower temperature. This together with the variation of $\langle l_c \rangle$ reduces the α parameter steadily at low temperature and the smectic phase is unstable except for very low temperature. Thus the lower homologs exhibit only the $I-N$ phase sequence down to quite low temperatures. As the homologous series is ascended, the system shows a tendency to exhibit smectic polymorphism, where at $N=6$, it shows the reentrant phase sequence $I-N-Sm-N_{re}$. For still higher homologs, α_{in} at T_{N-I} is quite high (Table II), but all-*trans* probability is low. At high temperature, the smectic phase is found to stabilize (Table II). However, due to the large number of conformations available, P_{tr} increases significantly with the lowering of temperature. This together with the variation of $\langle l_c \rangle$ induces a lowering of the α parameter that is not quite sufficient to destabilize the smectic phase. Consequently reentrance vanishes for the higher member. Variation of p_{tr} and $\langle l_c \rangle$ with temperature are shown for $N=4-7$ in Table III.

Thus our calculation on the nonpolar system demonstrates that a change in chain configuration with temperature may lead to reentrance. It should however be stat-

TABLE III. All-*trans* probability and average chain lengths for different members of the homologous series $T=300$ K, $r_c=r_{c0}+\Delta r$, $\Delta r=P_{tr}$ times the all-*trans* length equals $P_{tr}l_{tr}$, $\langle l \rangle=r_{c0}+\langle l_c \rangle$, $\langle l_c \rangle$ denotes the average length of chain, N denotes the number of chain segments, $r_{c0}=2.0$ and $K_c=0.6405$.

\mathcal{F}	$N=4$ $L_{tr}=4.7492$			$N=5$ $L_{tr}=5.4984$			$N=6$ $L_{tr}=7.4984$			$N=7$ $L_{tr}=8.2476$		
	P_{tr}	$\langle l_c \rangle$	$K_c r_c / \langle l \rangle$	P_{tr}	$\langle l_c \rangle$	$K_c r_c / \langle l \rangle$	P_{tr}	$\langle l_c \rangle$	$K_c r_c / \langle l \rangle$	P_{tr}	$\langle l_c \rangle$	$K_c r_c / \langle l \rangle$
1.0	0.278	1.73	0.569	0.154	2.32	0.422	0.085	2.90	0.344	0.043	3.0	0.302
1.2	0.313	1.81	0.586	0.168	2.38	0.483	0.106	3.06	0.353	0.050	3.18	0.298
1.4	0.348	1.87	0.603	0.213	2.56	0.445	0.130	3.22	0.365	0.062	3.34	0.301
1.6	0.384	1.93	0.622	0.246	2.68	0.458	0.157	3.34	0.381	0.076	3.47	0.308
1.8	0.421	1.99	0.651	0.281	2.80	0.473	0.187	3.48	0.398	0.092	3.61	0.315
2.0	0.458	2.06	0.658	0.316	2.92	0.487	0.220	3.62	0.415	0.110	3.75	0.324
2.2	0.496	2.10	0.677	0.356	3.04	0.503	0.255	3.74	0.436	0.13	3.89	0.335
2.4	0.532	2.16	0.696	0.395	3.16	0.517	0.293	3.88	0.457	0.154	4.04	0.346
2.6	0.568	2.20	0.716	0.434	3.28	0.532	0.332	4.00	0.479	0.178	4.18	0.349
2.8	0.603	2.26	0.731	0.474	3.40	0.546	0.373	4.14	0.500	0.205	4.33	0.373
3.0	0.637	2.30	0.755	0.513	3.50	0.562	0.414	4.24	0.524	0.234	4.48	0.388
3.2	0.669	2.34	0.764	0.552	3.62	0.574	0.455	4.36	0.544	0.265	4.62	0.404
3.4	0.70	2.38	0.778	0.589	3.72	0.587	0.496	4.46	0.567	0.297	4.78	0.420
3.6	0.728	2.42	0.791	0.624	3.82	0.598	0.536	4.56	0.587	0.332	4.94	0.437
3.8	0.755	2.46	0.802	0.659	3.90	0.610	0.575	4.64	0.608	0.367	5.08	0.435

ed that our calculation is based on very drastic assumptions and that reentrance has been obtained only for well-chosen values of some parameters. How well our model would relate to real systems is an open question. What the calculation indicates is that a gradual stiffening of chains may play a positive role in reentrant phenomenon. The encouraging aspect of this work is that reentrance is expected for certain intermediate members only. We may further conclude that chain flexibility may be one of the contributing factors for the observed reentrance in a nonpolar mixture.

It should be mentioned that we used the pair potential as in Eq. (1b) rather than the potential of Eq. (2) which can give rise to the downward slope of N - I curves with an increasing number of chain segments. The reason is that for flexible molecules the potential of Eq. (2) poses a problem—we cannot strictly assume that only n_z is

changing (as was done in Ref. 32 to reproduce a lowering of N - I transition temperature as a homologous series is ascended) from member to member and n_x and n_y are remaining constant irrespective of temperature. This is because gauche states are more probable at higher temperature and as a result a molecule sort of spreads out laterally.

In conclusion we would like to say that the above work supplements Dowell's lattice model for condensed phases²⁶⁻²⁹ for reentrance in systems of nonpolar molecules.

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*Permanent address: Scottish Church College, Calcutta 700 006, India.

†Permanent address: R.K. Mission Vidyamandira, Belur, West Bengal, India.

‡Permanent address: Saha Institute of Nuclear Physics, Calcutta 700 009, India.

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