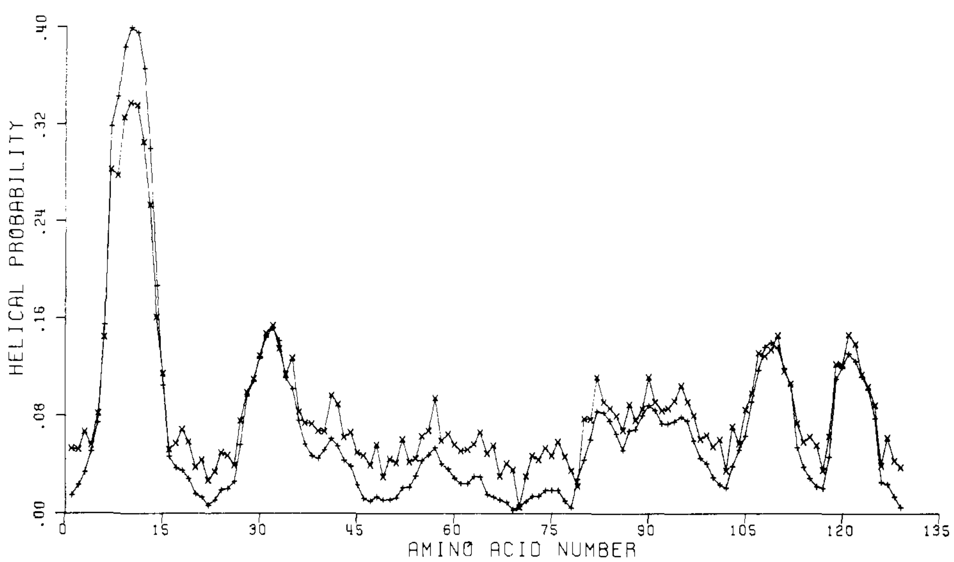

Figure 1. The helical probabilities for the amino acids in lysozyme computed using eq 1 (+) and eq 2 (X).

tistical weights assigned to those states. Dividing the numerator and denominator of the middle term of eq 3 by n_c, it is easy to see that

$$s = n_h/n_c \tag{4}$$

This is the same result obtained by Tanaka and Scheraga (see eq 16 of ref 1) whose formulation is in terms of the residue partition function. It should be noted that n_h/n_c is actually the equilibrium constant for the coil to helix transition and that under the above conditions the statistical weight, s, is equal to the equilibrium constant.

References and Notes

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Phenomenology of Short-Range Order in *n*-Alkane Liquids

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ABSTRACT: A fluctuation theory, analogous to de Gennes' treatment for the isotropic liquid crystal phase, is used to compute the effects of enhanced short-range orientational order in *n*-alkane liquids. Anisotropy of shape causes parallel alignment of neighboring chain segments. The segments may belong to the same or to different molecules. The free energy of the extra short-range order is reduced to explicit form by the introduction of two adjustable parameters, T^* and N^*. T^* is a pseudo-critical temperature, below the freezing point for the normal paraffins, at which the free energy density of orientationally ordered fluid would equal that of the disordered fluid if the volume of the liquid remained constant. It appears to be near the orthorhombic–hexagonal solid phase transition observed for *n*-alkanes which have an odd number of carbon atoms. N^* is proportional to the volume integral of the (asymptotic) orientational part of the pair segment correlation function. A compensation of energy and entropy effects is predicted. Both are negative and should behave as $-(T - T^*)^{-\gamma}$ where T is the absolute temperature and γ is expected to be close to one. Corroboration of the theory is found for the excess energy of mixtures of $n\text{-C}_{14}$ and $n\text{-C}_{16}$ with inert (noncorrelating) second components. For both alkanes, T^* is about 270 °K and N^* depends on the solute. The excess heat capacity of these mixtures is also computed, and agreement with experiment is reasonable. Small "anomalous" increments in the expansion coefficient and compressibility of the pure liquid *n*-alkanes are anticipated. Effects of the correlation of segment orientations (CSO) on optical properties are briefly discussed. Both the magnetic birefringence and the intensity of depolarized Rayleigh scattering should display a contribution from the CSO which increases strongly with the approach to the freezing point as $(T - T^*)^{-\gamma}$.

The detailed local structure of simple fluids is determined primarily by the repulsive forces acting between the molecules.[1] Attractive forces act over greater distances and do not produce sharp, short-range effects. Repulsive forces should also govern local structure in complex fluids. This is partially verified for liquid crystals where Onsager has shown that the excluded volume between rigid cylinders is able to induce a transition to a fluid phase with long-range orientational order.[2] The important role of the attractive potential in liquid crystals is believed to be a stabilization of the regions of molecular alignment.[3] The excluded volume force between the molecules is reduced by bringing them into a more parallel arrangement, and this permits a closer approach and a resultant lowering of the potential energy.

Barring an unexpected cancellation of repulsions and long-range attractions, chain-molecule systems should exhibit some degree of cooperative parallel correlation, even in the fluid phase. Wulf and De Rocco have presented a model calculation showing that a fluid of purely semiflexible molecules can undergo a liquid crystal transition for certain (not unphysical) values of the length-to-breadth ratio and flexibility.[4] Owing to the rotational freedom which the member segments possess, orientational ordering is not expected to persist for the entire chain length. Bothorel and co-workers have called the local order in the *n*-alkanes and *n*-alkane-like systems a correlation of molecular orientations (CMO).[5] To emphasize the limited range of order down a single chain, it shall be referred to in this article as a correlation of *segmental* orientations (CSO).

Evidence of CSO in linear alkanes is plentiful.[6] Examination of thermal behavior suggests an order contribution to both the enthalpy and heat capacity.[7,8] Depolarized Rayleigh scattering provides evidence of orientational correlations in the pure liquid alkanes, as well as in their mixtures.[5] Since the alkanes are true isotropic liquids, the order is local and not a macroscopic property of the system. (In the solid phase and in oil slicks or lipid membranes, there is long-range orientational order which is a macroscopic property of the phase.) The thermodynamic average of the order must vanish in the absence of mechanical or electromagnetic stresses. The alkanes are nonpolar so the order is invariant to reflection. Short-range order fluctuations with these properties occur in the isotropic phase of liquid crystals.[9] This article presents a theory of CSO in chain-molecule fluids analogous to the de Gennes' fluctuation theory of the isotropic liquid crystal phase.[10,11]

A significant enhancement of the usual short-range order is found in systems about to undergo a critical or near-critical phase transition.[12] At a critical point the difference in energy and entropy of the two phases vanishes and the correlation length for the order fluctuations is infinite. In the vicinity of the transition, the free energy barrier separating the two phases is small, and fluctuations readily occur. It is possible to discuss this critical pretransition region phenomenologically, as did Landau and Lifshitz,[13] by defining a local free density and computing from it corrections to the thermodynamic properties arising from the phase fluctuations. Though open to criticism from several sides,[12] the Landau–Lifshitz approach, supplemented by the Ornstein–Zernicke treatment of the correlation in fluctuations,[14] provides an intuitive, semiquantitative treatment of the critical region.

The arguments which Landau and Lifshitz applied to a real critical transition can as well be made for a system which undergoes a weak first-order phase transition. Here too, in the region preceding the transition, the free energy barrier to fluctuations is small, and they can be expected therefore to get large steadily with the approach to the transition point. (Note that in both cases the theory is applied to the system *above* the transition where there is a true nonzero difference in the free energy density of the two phases.) This approach has been highly successful in discussing the statics and dynamics of orientational correlations in liquid crystals in the region above the nematic transition.[11,12] In this article the same ideas are advanced to explain some of the observed properties of the liquid *n*-alkanes in the region preceding solidification. The experimental facts seem consistent with a local orientation order, which grows dramatically with falling temperature. This suggests that the barrier to fluctuations in order behaves in a fashion similar to the barrier in liquid crystals. This provides the motivation for the fluctuation theory of CSO employed. There is no doubt that the freezing transition is first order, and strongly so, but the existence of several solid–solid phase transitions in solid paraffins suggests that the coupling of the rotational and translational phase transitions is weak.

A functional expansion of the free energy of the fluid is first introduced. The magnitude of the long-wavelength fluctuations is computed in terms of the kernel of the free energy expansion. A simple model of the kernel, reminiscent of that used for liquid crystals, is introduced to predict the temperature dependence of the fluctuations. Explicit formulas for the free energy, energy, and entropy of the order result. Comparison with experiment is made for several alkane mixtures. Conclusions about the range of CSO and other effects likely to be consequence of enhanced local orientational order are discussed.

Static Correlations in Segment Orientations (CSO)

We first present the formalism of the correlations in segment orientations. The physical idea is that segment correlation is growing beyond the normally expected nearest neighbor (or perhaps next nearest neighbor) limit and becoming increasingly longer ranged. The net result is that the segment–segment pair correlation function can be imagined to consist of a short-ranged part which is not too dependent on temperature, etc., in the vicinity of the freezing point, and a "long-range" (third, fourth neighbor) part which is growing in importance with the approach to the transition. The calculation is intuitive, or rather phenomenological in character. Equation 18 is the fundamental result and represents the effective "Landau Hamiltonian" for the problem at hand. It describes the energetics of a system where local, very short-range behavior has been averaged over. It could be arrived at by using renormalization group methods,[15] but no attempt has been made here to derive (18) from a molecular statistical model. We prefer instead to start from a simpler, functional derivative approach which has proven useful in discussing order fluctuations in liquid crystals.[16]

Workman and Fixman have presented a general formalism to describe angular correlations in fluids.[17] The central result of their method is an expression for the Helmholtz free energy difference between two states of the fluid:

$$\begin{aligned}\beta(A - A_0) = \int \mathrm{d}\mathbf{r}_1\, \mathrm{d}\mathbf{e}\, \{&\rho(\mathbf{r}_1,\mathbf{e}) \ln [\rho(\mathbf{r}_1,\mathbf{e})/\rho^*(\mathbf{r}_1,\mathbf{e})] \\ &- \rho(\mathbf{r}_1,\mathbf{e}) + \rho^*(\mathbf{r}_1,\mathbf{e}) + \beta U(\mathbf{r}_1,\mathbf{e})\rho \\ &- \tfrac{1}{2}\int \mathrm{d}\mathbf{r}_2\, \mathrm{d}\mathbf{e}'\, C^*(\mathbf{r}_1,\mathbf{e};\mathbf{r}_2,\mathbf{e}')\Delta(\mathbf{r}_1\mathbf{e})\Delta(\mathbf{r}_2,\mathbf{e}')\}\end{aligned} \quad (1)$$

where A is the free energy, A_0 is the free energy in the reference state, $\rho(\mathbf{r},\mathbf{e})$ is the density of particles at $\mathbf{r}$ in the direction $\mathbf{e}$, $\rho^*(\mathbf{r},\mathbf{e})$ is the same density in the reference state, $U(\mathbf{r},\mathbf{e})$ is an external potential acting on a particle at $\mathbf{r}$ in the direction $\mathbf{e}$, $C^*(\mathbf{r}_1,\mathbf{e};\mathbf{r}_2,\mathbf{e}')$ is the direct correlation function in the reference state , β is $1/kT$, and Δ is $\rho(\mathbf{r},\mathbf{e}) - \rho^*(\mathbf{r},\mathbf{e})$. This result becomes relevant to fluids of chain molecules if the particle density ρ is reinterpreted as a *segment* density. The normalization of the segment density ρ is

$$\int\int \mathrm{d}\mathbf{r}\, \mathrm{d}\mathbf{e}\, \rho(\mathbf{r},\mathbf{e}) = Ln = N \quad (2)$$

where n is the average number of molecules in the system, L is the number of segments per molecule, and N is the average number of segments in the system. In eq 1 the direct correlation function has been approximated by the first term in its functional Taylor series expansion.[17] Physically, this approximation means that eq 1 is valid for states sufficiently close to the reference state. The reference state in the present application of the theory is the pure alkane liquid with no fluctuations in segment density except very local (nearest neighbor) ones. In this case

$$\rho^*(\mathbf{r},\mathbf{e}) = \bar{\rho}/4\pi \quad (3)$$

where $\bar{\rho}$ is the average number density of segments in the liquid. The fluid with enhanced local correlations of segment orientations (CSO) will have a different free energy from this reference state. The magnitude of the free energy difference, for an arbitrary state of local fluctuation given by $\rho(\mathbf{r},\mathbf{e})$, can be computed from eq 1. The thermal averages of the fluctuations are found by averaging over all states of fluctuation at a temperature T with a Boltzmann factor equal to the free energy difference in eq 1.[13]

To simplify the calculations, the logarithm in eq 1 is first expanded

$$\beta(A - A_0) = \tfrac{1}{2}\int d\mathbf{r}_1\, d\mathbf{r}_2\, d\mathbf{e}\, d\mathbf{e}' \left[\frac{\delta(\mathbf{r}_1 - \mathbf{r}_2)\delta(\mathbf{e} - \mathbf{e}')}{\rho^*} - C^*(\mathbf{r}_1,\mathbf{e};\mathbf{r}_2,\mathbf{e}')\right] \Delta(\mathbf{r}_1,\mathbf{e})\Delta(\mathbf{r}_2,\mathbf{e}') + \ldots \quad (4)$$

where U has been set equal to zero, and $\delta(\mathbf{r} - \mathbf{r}')$ and $\delta(\mathbf{e} - \mathbf{e}')$ are Dirac δ functions. Retaining only the first term in eq 4, and introducing the quantity

$$c(\mathbf{r}_1,\mathbf{e};\mathbf{r}_2,\mathbf{e}') = \frac{\delta(\mathbf{r}_1 - \mathbf{r}_2)\delta(\mathbf{e} - \mathbf{e}')}{\rho^*} - C^*(\mathbf{r}_1,\mathbf{e};\mathbf{r}_2,\mathbf{e}') \quad (5)$$

the free energy increment can be written

$$\beta(A - A_0) = \tfrac{1}{2}\int d\mathbf{r}_1\, d\mathbf{r}_2\, d\mathbf{e}\, d\mathbf{e}'\, c(\mathbf{r}_1,\mathbf{e};\mathbf{r}_2,\mathbf{e}')\Delta(\mathbf{r}_1,\mathbf{e})\Delta(\mathbf{r}_2,\mathbf{e}') \quad (6)$$

If there are any cooperative fluctuations in the fluid, they will be slowly varying in space since otherwise their excitation energy will be much larger than kT. In terms of eq 6, this means that there must be particular combinations of fluctuations $\Delta(\mathbf{r},\mathbf{e})$ for which the free energy barrier, measured by $c(\mathbf{r}_1,\mathbf{e};\mathbf{r}_2,\mathbf{e}')$, is small. The important physical quantities to be identified are the size and energy of the fluctuations. The size of the fluctuations is determined by the $\mathbf{r}$ dependence of c. This is best found experimentally through a study of the angular dependence of light scattered by the system. Unfortunately this information does not appear to be available at present, but should be soon.[18] The experimental data at hand are largely thermodynamic. It can be accounted for simply in terms of the number N^* of modes of fluctuation which are thermally excited in the temperature range near solidification, and T^*, a pseudocritical temperature at which long-range orientational order would set in if the freezing transition did not intervene. These parameters are here taken as adjustable, though in principle they might be found from a molecular model in the manner of Workman and Fixman.[17] An additional benefit from the molecular model of c would be its spatial dependence.

Next we introduce a virtual lattice of simple cubic cells which permits the very short ranged fluctuations to be preaveraged over, allowing a separate treatment of the more slowly varying correlations which are the interest here.[15] Let the total volume V be divided into M^3 cells of equal volume. The volume of a cell should be chosen much larger than a molecular volume but smaller than the total volume of the system. A simple cubic lattice spanning the system volume permits the introduction of integral lattice vectors $\mathbf{m}$ to locate the position of each cell. Each lattice vector is written

$$\mathbf{m} = m_1\mathbf{x} + m_2\mathbf{y} + m_3\mathbf{z} \quad (7)$$

where m_1, m_2, m_3 are integers between 0 and $m - 1$ and $\mathbf{x}$, $\mathbf{y}$, $\mathbf{z}$ are unit vectors defining the primitive translations of the simple cubic lattice. The purpose of introducing the lattice is to allow preaveraging. Let us suppose that the short-range interactions have been averaged over in each cell and that the orientational configuration of each cell can be specified by giving the singlet density $\rho(\mathbf{r},\mathbf{e})$ in a given cell. The volume integrations in eq 6 can then be replaced by summations over the cell-dependent quantities. This is accomplished using the identification

$$\int d\mathbf{r} \rightarrow \frac{V}{M^3}\sum_{\mathbf{m}} \quad (8)$$

where V/M^3 is the volume per cell. Equation 6 becomes

$$\beta(A - A_0) = \tfrac{1}{2}\left(\frac{\mathrm{V}}{\mathrm{M}^3}\right)^2 \times \sum_{\mathbf{m}}\sum_{\mathbf{m}'} \int d\mathbf{e}\, d\mathbf{e}'\, c(\mathbf{m} - \mathbf{m}',\mathbf{e},\mathbf{e}')\Delta(\mathbf{m},\mathbf{e})\Delta(\mathbf{m}',\mathbf{e}') \quad (9)$$

Going over to finite Fourier transforms

$$\Delta(\mathbf{m},\mathbf{e}) = M^{-3/2}\sum_{\mathbf{p}} \int \rho(\mathbf{p},\mathbf{e})e^{2\pi i\,\mathbf{p}\cdot\mathbf{m}} \quad (10)$$

$$c(\mathbf{m}_1 - \mathbf{m}_2,\mathbf{e},\mathbf{e}') = M^{-3}\sum_{\mathbf{p}} \tilde{c}(\mathbf{p},\mathbf{e},\mathbf{e}')e^{2\pi i\,\mathbf{p}\cdot(\mathbf{m}_1-\mathbf{m}_2)} \quad (11)$$

where the $\mathbf{p}$ are reciprocal lattice vectors, the free energy becomes

$$\beta(a - A_0) = \tfrac{1}{2}\left(\frac{\mathrm{V}}{\mathrm{M}^3}\right)^2 \sum_{\mathbf{p}} \int d\mathbf{e}\, d\mathbf{e}'\, \tilde{c}(\mathbf{p},\mathbf{e},\mathbf{e}')\tilde{\rho}(\mathbf{p},\mathbf{e})\tilde{\rho}^*(\mathbf{p},\mathbf{e}') \quad (12)$$

where the summation is over all $\mathbf{p}$.

The order parameter commonly employed for liquid crystals is

$$\bar{s} = \langle 1/2(3\cos^2\theta - 1)\rangle \quad (13)$$

where the brackets denote a thermal average taken over the whole system, and θ is the angle between a molecule's axis and the direction of preferential alignment. $\bar{s}$ is also the order parameter used to describe orientational correlations of hydrocarbon chains in lipid bilayers.[19] In an alkane liquid or solution there is no preferred direction and $\bar{s}$ is zero. But the average *squared* order,

$$\bar{s}^2 = \langle 1/2(3\cos^2\theta - 1)\cdot 1/2(3\cos^2\theta - 1)\rangle \quad (14)$$

is not zero. For chain-molecule systems, where there is no single molecular axis, the appropriate measure of correlation is $\bar{s}^2$, defined as in eq 14 where θ is the angle between a *segmental* axis and some fixed axis. For such systems, each segment of the molecule has its own order parameter. Though a strong correlation between segmental order and molecular order exists for hydrocarbon chains in bilayers, and in fluids of small semirigid molecules, it is markedly less in chain-molecule liquids and polymer solutions and melts. In this article $\bar{s}^2$ refers to segmental and not to molecular order.

To compute $\bar{s}^2$ (rather the long-wavelength, slowly varying part) with the aid of eq 12, it is convenient to assume that $\tilde{c}(\mathbf{p},\mathbf{e},\mathbf{e}')$ depends only on the magnitude of the vector $\mathbf{p}$ and on the scalar product $\mathbf{e}\cdot\mathbf{e}'$. As Workman and Fixman point out,[17] this is equivalent to taking only the first term in a spherical harmonic expansion. They cite evidence that supports this approximation for the pair interaction energy of nonspherical molecules. The expansion of $\tilde{c}(\mathbf{p},\mathbf{e},\mathbf{e}')$ in Legendre polynomials P_l (cos ϕ), where $\mathbf{e}\cdot\mathbf{e}' = \cos\phi$, is

$$\tilde{c}(p,e,e') = \sum_{l=0}^{\infty} \tilde{c}_l(p)P_l(\cos\phi) \quad (15)$$

and likewise for the Fourier components $\tilde{\rho}(\mathbf{p},\mathbf{e})$

$$\tilde{\rho}(p,e) = (4\pi)^{-1}\sum_{l=0}^{\infty} \tilde{\rho}_l(p)P_l(\cos\theta_1) \quad (16)$$

When eq 15 and 16 are substituted into eq 12, and the integrations over angles performed, the expression for the free energy difference due to CSO becomes

$$\beta(A - A_0) = \tfrac{1}{2}\left(\frac{V}{M^3}\right)^2 \sum_{\mathbf{p}}\sum_{l=0}\left(\frac{1}{2l + 1}\right)^2 \tilde{c}_l(\mathbf{p})\tilde{\rho}_l(\mathbf{p})\tilde{\rho}_l^*(\mathbf{p}) \quad (17)$$

Two remarks about eq 17 are appropriate. First, fluctuations with different wave vectors $\mathbf{p}$ are independent since their free energies are additive. This approximation enters when eq 1 is restricted to quadratic terms only. Unless the quantities $\tilde{c}_l(\mathbf{p})$ get small (which they should not do for the alkanes) this is not a serious limitation. Second, fluctuations with different symmetries, i.e., different values of l, are uncoupled. This is a direct consequence of the assumption that the kernel $\tilde{c}$ depends only on the magnitude of $\mathbf{p}$ and on the scalar product $\mathbf{e}\cdot\mathbf{e}'$. A more general dependence must be allowed if a treatment of density-order coupling is attempted.[16] They are ignored at present.

The local segmental order in the liquid is defined to be

$$s(\mathbf{m}) = \frac{\int \mathrm{d}\mathbf{e}\, P_2(\cos\theta)\rho(\mathbf{m},\mathbf{e})}{\int \mathrm{d}\mathbf{e}\rho(\mathbf{m},\mathbf{e})} \qquad (18)$$

where $P_2(\cos\theta) = 1/2(3\cos^2\theta - 1)$ is the second-order Legendre polynomial, θ is the angle between the segmental axis and some fixed axis, and $\rho(\mathbf{m},\mathbf{e})$ is the singlet segmental density in cell $\mathbf{m}$. The segment density $\rho(\mathbf{m},\mathbf{e})$ has the expansion

$$\rho(\mathbf{m},\mathbf{e}) = (4\pi)^{-1} \sum_{l=0}^{\infty} \rho_l(\mathbf{m})P_l(\cos\theta) \qquad (19)$$

Substituting eq 19 into eq 18 and integrating, we obtain

$$s(\mathbf{m}) = \rho_2(\mathbf{m})/5\rho_0(\mathbf{m}) \qquad (20)$$

where $\rho_0(\mathbf{m})$ is the number density of segments in cell $\mathbf{m}$. This is taken equal to the average number density $\bar{\rho}$. The average squared order $\bar{s}^2$ can be computed from the transformed variables $\tilde{\rho}_2(\mathbf{p})$;

$$\langle s(\mathbf{m})s(\mathbf{m}')\rangle = M^{-3} \sum_{\mathbf{p}} \sum_{\mathbf{p}'} \langle \tilde{\rho}_2(\mathbf{p})\tilde{\rho}_2(\mathbf{p}')\rangle c^{2\pi i(\mathbf{p}\cdot\mathbf{m}+\mathbf{p}'\cdot\mathbf{m}')} \qquad (21)$$

where, as before, the angular brackets denote thermal averages. The thermal averages are computed assuming the probability of a state of fluctuation is proportional to its free energy.[13] Formally, then we have

$$P(\{\tilde{\rho}\}) = Q \exp[-\beta(A - A_0)] \qquad (22)$$

where P is the probability of a given state of fluctuation, specified by the collection of cell densities $\{\tilde{\rho}\}$, Q is a normalization factor and $\beta(A - A_0)$ is the difference in free energy between the two states divided by kT. Using eq 17 and 22, the squared fluctuations become

$$\langle \tilde{\rho}_l(\mathbf{p})\tilde{\rho}_{l'}(\mathbf{p}')\rangle = (\beta w(\mathbf{p},l))^{-1}\delta_{\mathbf{p},-\mathbf{p}'}\delta_{l,l'}G(\mathbf{p},l) \qquad (23)$$

where

$$\beta w(\mathbf{p},l) = \left(\frac{V}{M^3}\right)^2 \left[\frac{\tilde{c}_l(\mathbf{p})}{(2l+1)^2}\right] \qquad (24)$$

and

$$G(\mathbf{p},l) = \left(1 - \frac{x}{e^x - 1}\right);\ x = \frac{w(\mathbf{p},l)}{kT}\,[\tilde{\rho}_l{}^{\max}(\mathbf{p})]^2 \qquad (25)$$

and the δ are Kronecker δ functions. The function $G(\mathbf{p},l)$ ensures that eq 23 does not produce nonsense as $w(\mathbf{p},l)$ goes to zero. If in fact the upper limit on the Fourier components $\tilde{\rho}_l$ is taken to infinity, then $G(\mathbf{p},l) = 1$. This is the approximation often made.[12,15] If the interest is entirely in the correlation functions near a critical point, then $G(\mathbf{p},l)$ is of negligible importance. Here, however, we are attempting to estimate the energy, etc., which are essentially integrals of the correlation functions. In this case due attention must be paid to $G(\mathbf{p},l)$.

The spatial correlation function of the order from cell to cell (eq 21) now becomes

$$\langle s(\mathbf{m})s(\mathbf{m}')\rangle = M^{-3}kT \sum_{\mathbf{p}} [w(\mathbf{p},2)]^{-1}e^{2\pi i\,\mathbf{p}\cdot(\mathbf{m}-\mathbf{m}')}G(\mathbf{p},2) \qquad (26)$$

In particular, the squared order may be written

$$\bar{s}^2 = \langle s^2(\mathbf{m})\rangle = M^{-3}kT \sum_{\mathbf{p}} [w(\mathbf{p},2)]^{-1}G(\mathbf{p},2) \qquad (27)$$

The primary task of a statistical mechanical theory of chain-molecule liquids would be calculation of $w(p,2)$ from a molecular model. We hope to consider this avenue of approach in the near future. For the present we are content to explore the thermodynamic consequences of a simple model of w, based not on a molecular model, but rather on the analogy here proposed between the enhanced local order in liquid alkanes and pseudocritical fluctuations which occur in liquid crystals near the transition to the ordered fluid phase.

A Simple Model of $w(p,2)$

In the theory of order fluctuations occurring above critical transitions, Landau and Lifshitz[13] assumed that the barrier to the fluctuations, the quantity analogous to $w(p,2)$ in eq 27, vanished as the transition temperature was approached. De Gennes[10] used the method of Landau and Lifshitz to compute the augmented static orientational fluctuations above the nematic-liquid crystal transition. Though the barrier to the fluctuations is known not to vanish (the transition is unquestionably first order), experiment has amply confirmed that the fluctuation behavior is accounted for by assuming the following functional form for $w(p,2)$:

$$w(p,2) = a(T - T^*) + bp^2 + \ldots \qquad (28)$$

where a and b are practically contants through the transition region and T^* is a pseudo-critical temperature somewhat below the actual nematic-isotropic transition temperature. As a first approximation to the behavior of the (long wavelength) orientational fluctuations in the liquid alkanes near solidification, $w(p,2)$ of eq 26 and 27 is taken to have the same form given in eq 28 for liquid crystals. The major differences expected are that a will be larger and T^* will be further below the transition point than the analogous quantities for a true liquid crystal.[20]

Having adopted eq 28, it remains to be shown how the fluctuation contributions to the free energy, etc., can be computed. Assuming that only $\bar{s}^2$ contributes to the excess thermal properties, eq 17 can be written

$$A - A_0 = (1/2) \sum_{p} w(p,2)|\tilde{\rho}_2(\mathbf{p})|^2 \qquad (29)$$

where the factor $(kT)^{-1}$ is now included in $w(p,2)$. One sees that as the temperature is lowered, the amount of free energy associated with a given magnitude of fluctuation $|\tilde{\rho}_2(\mathbf{p})|$ gets less since, from eq 28, $w(p,2)$ is getting smaller. The thermal average of the excess free energy is found from eq 29 and eq 23

$$\langle A - A_0\rangle = (kT/2) \sum_{p} G(p,2) \qquad (30)$$

The summand in eq 30 is the product of two quantities, $w(p,2)$ and $\langle|\tilde{\rho}_2|^2\rangle$. The first is a decreasing function of temperature and the second increasing. We assume that $G(p,2)$ is a weak function of temperature and parameterize the sum

$$\sum_{p} G(p,2) \equiv N^* \qquad (31)$$

Henceforth the temperature dependence of N^* will be ignored, though in a more refined calculation it could be determined in terms of a, b, T^*, M^3, V, and $|\tilde{\rho}_2|^{\max}$. N^* will be assumed to be an adjustable parameter, to be determined from experiment. It is readily accessible to experiment since the excess free energy is

$$\langle A - A_0\rangle = (kT/2)N^* \qquad (32)$$

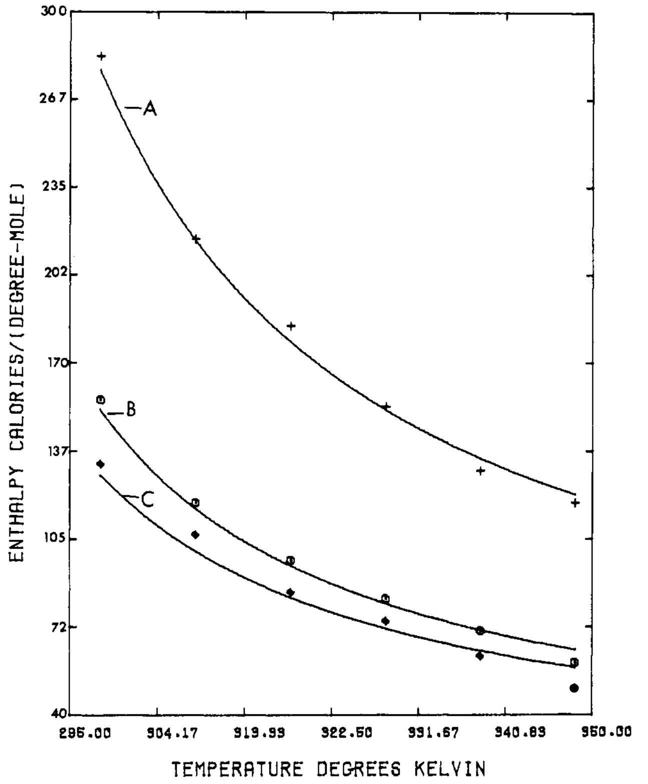

Figure 1. Excess enthalpies of mixing as a function of temperature for some binary systems of n-alkanes in noncorrelating solutes. The symbols are the experimental values of H_{excess} from ref 8b divided by $x_A x_B$, where x_A is the segment fraction of alkane and x_B is the segment fraction of component 2. The solid curves are theoretical excess energies of CSO from eq 35, using the values of T^* and N^* shown in Table I: (A) n-C_{16} in 2,2,4,4,6,8,8-heptamethylnonane (+); (B) n-C_{16} in 2,6,10,15,19,23-hexamethyltetracosane(squalane) (⊙); (C) n-C_{14} in squalane (◊).

It can be thought of as the number of thermally excited long wavelength order fluctuations.

Let $S - S_0$ be the difference in entropy between a state with extra orientational correlations and the reference state which has only the normal, very short-range deviations. It is computed from the free energy in the usual way:

$$S - S_0 = -\left[\frac{\partial(A - A_0)}{\partial T}\right]_V \tag{33}$$

The part of $w(p,2)$ that dominates the thermal behavior of the fluctuations is $a(T - T^*)$, while the second term in eq 28, bp^2, determines the spatial extent and decay of them. Since light scattering measurements are not yet available from which to determine b,[18] it is permissible to ignore it for the present, especially since surprisingly simple thermodynamic formula then result. Taking the temperature derivative of $A - A_0$ in eq 29 and forming the thermal averages over the fluctuations, the final expressions for the excess thermal properties of the fluid can be written:

$$\langle S - S_0\rangle \simeq -0.5kN^*(1 - T^*/T)^{-1} \tag{34}$$

$$\langle E - E_0\rangle \simeq 0.5kN^*\{1 - (1 - T^*/T)^{-1}\} \tag{35}$$

where the temperature dependence of $G(p,2)$, and hence of N^*, and the wave vector dependence of $w(p,2)$ have been ignored. To the same degree of approximation, the excess heat capacity due to the static orientation correlations is

$$\langle C_V - C_{V0}\rangle \simeq \frac{-0.5kN^*(T^*)^2}{(T - T^*)^2} \tag{36}$$

Table I
Ordering Temperature (T^*) and Excitation Number (N^*) for n-C_{14} and n-C_{16} Mixtures

System	T^*, deg abs.	$N^* = \overline{M}^3$
Squalene and n-C_{16}	270	1.63×10^{22}
Heptamethylnonane and n-C_{16}	268	3.13×10^{22}
Squalene and n-C_{14}	267	1.54×10^{22}

Experimental Section

To compare the above formulas with experiment, it would be desirable to have measurements of the CSO contribution to the thermal properties of the pure liquid alkanes.[21] Since these are not readily available, data for enthalpies and heat capacities of alkane mixtures are considered. Croucher and Patterson[8b] have examined several binary alkane mixtures with a view to isolating the effects of molecular correlation. There are clearly causes other than CSO which produce excess heats and heat capacities, most notably differences in free volume brought about by mixing.[22] However, several long alkanes, n-C_{14} and n-C_{16}, show particularly pronounced positive heats of mixing and negative excess heat capacities of mixing, yet the volume changes observed are very small (with the solvents used). For simplicity, we shall assume that all of the excess enthalpy and heat capacity observed by Croucher and Patterson for the n-C_{14} and n-C_{16} mixtures[8b] is due to CSO.

The heats of mixing were observed to be a symmetric function of the segment fraction of alkane. A simple lattice model of binary solutions[23] would give the energy of mixing as

$$\Delta E_{\text{mix}} = -0.5c\epsilon x_A x_B \tag{37}$$

where c is the coordination number of each species, $\epsilon = \epsilon_{AA} + \epsilon_{BB} - 2\epsilon_{AB}$, the difference in pair energies between the pure components and a pair of mixed molecules, and x_A and x_B are the fractions of components A and B. The quantity ϵ is a measure of the energy difference between the pure components and the mixture. It is unusually negative for the long alkanes (it costs energy to separate the alkane molecules from each other) when they are mixed with some spherical solvent molecules. The reason proposed by Croucher and Patterson is that correlation is lost upon going to the mixture, with an attendant loss in configuration energy. Molecules of different sizes and shapes, especially spherical, interfere with angular correlations and destroy the favorable mutual alignment. We shall accept this interpretation of the data and use eq 35 to attempt to account for the temperature behavior.

Equation 37 is used to estimate the CSO energy of the pure alkane. Segment (volume) fractions are used for x_A and x_B. All of the exchange energy is assigned to the correlations, though this is doubtlessly a crude assumption. The experimental excess enthalpies of mixing are shown in Figure 1 for three different n-alkane systems. Also shown are theoretical curves from eq 35 using the parameters T^* and N^* given in Table I. These values were obtained by fitting $\Delta E_{\text{mix}}/x_A(1 - x_A)$ to eq 35, where x_A is the segment fraction of alkane. Equation 36 for the excess heat capacity contains no new parameters. In Figure 2 are shown calculated and experimental excess heat capacities for the same three alkane mixtures.

Discussion

The qualitative and quantitative agreement between experiment and theory is encouraging. The mathematical form of the energy effect is well described. The heat capacities are not as good, but this is expected since second derivatives of the free energy are much more sensitive to the approximations. The sign of the heat capacity effect, and its sharp temperature dependence, are qualitatively correct. The hypothetical ordering temperatures T^* are 20 to 30 °C below the freezing points. It is perhaps significant that a solid–solid transition occurs in n-C_{15} at 270.9 K.[24] The high-temperature phase is hexagonal, with a considerable degree of rotational freedom, whereas the low-temperature orthorhombic phase has greatly restricted chain rotation. Such a solid phase transition is not observed for alkanes with an even number of carbon atoms, though it is seen for normal alkanes with an odd number of carbons starting with n-C$_9$.[24] n-C$_{14}$ and n-C$_{16}$ freeze directly to triclinic structures where rotation is restricted. The melting temperatures are 279 and 291 K, respectively. Perhaps the onset of long-range translational order "interrupts" the rotational condensation process. Instead of rotational order setting in naturally at T^*, it is hastened at freezing by the finite volume change which occurs there. The extra entropy loss for the even numbered alkanes on freezing shows up in their larger enthalpy of melting compared to the odd-numbered n-alkanes. It is 2–4 kcal typically.[24] This magnitude is consistent with the accumulated CSO energy which would be found from eq 35 in the vicinity of T^*;

$$T \sim T^* \sim 1 \text{ K}, \Delta E \sim N^*(T^*)^2 \sim 3600 \text{ cal/mol} \qquad (38)$$

Altogether, there seems to be some reason to expect that CSO in alkane liquids is related to the solid–solid transitions in the paraffins, especially to the orthorhombic → hexagonal transition among the even n-alkanes.

The parameter N^* depends on the solvent. Both squalane and heptamethylnonane destroy CSO upon dissolving the alkanes. N^* changes since the correlation length changes, yielding a different sum (or integral) in eq 31. The heat of mixing is positive because the energetically favorable alignment of segments is disrupted. Heptamethylnonane is twice as destructive of the order as squalane, perhaps because of its more globular shape.

The theory predicts a negative entropy of the CSO which grows more negative with falling temperature. This extra entropy, added to the energy, nearly cancels the latter. The free energy of the CSO is small and a weak function of temperature according to eq 32. Such a "compensation effect" has been verified by Croucher and Patterson[8b] for several mixtures containing n-C$_{16}$. The enthalpy and entropy of order were estimated for five systems. Plotted against each other, the energy and the entropy seem to lie on a straight line with a reciprocal slope close to 270 K, the value of T^* found here for n-C$_{16}$. Furthermore, the intercept of this line is close to zero, implying a nearly complete cancellation of entropy and energy effects. The present theory (see eq 32) predicts an intercept of $(N^*kT/2)$. From Table I, it is found that for n-C$_{14}$ and n-C$_{16}$, $(N^*kT/2) \sim$ 15–30 cal/mol. Two intercepts are found for Figure 4 of ref 8b, depending on whether volume or segment fractions are used to compute the energy and entropy of the ordering. They are 12 and 18 cal/mol. This is reasonably good agreement with the theoretical estimate. We note that N^* might be obtained from vapor pressure measurements above the liquids.

Other thermal properties might be expected to exhibit "pretransitional" anomalies if the static orientational correlations are getting large in the liquid alkanes as the temperature lowers. Because of more efficient packing, CSO regions will be more dense than the isotropic fluid, and density fluctuations should accompany the order fluctuations. Density fluctuations can lead to anomalies in both thermal expansion and compressibility.[16] There is some evidence of an increase in the thermal expansion coefficient of the n-alkanes near freezing.[25,26] The effect is definitely smaller than that seen in real liquid crystals above the nematic transition, and this could be the result of the shorter range of the alkane correlations.

Other evidence of angular correlation can come from optical studies. Depolarized Rayleigh scattering has already been mentioned (see ref 18). Temperature studies of the Cotton–Mouton constant have given evidence of enhanced pretransitional fluctuations in liquid crystals.[11] Similar studies do not seem to have been made for the n-alkanes. Pretransitional anomalies in the flow birefringence of the alkanes have been claimed[27] and denied.[28] It is probable that "parasitic" effects, similar to those responsible for the absense of anomalies for the optical Kerr effect in liquid crystals (local field, density corrections, etc.),[11] can render the detection of the orientational correlation effect difficult.

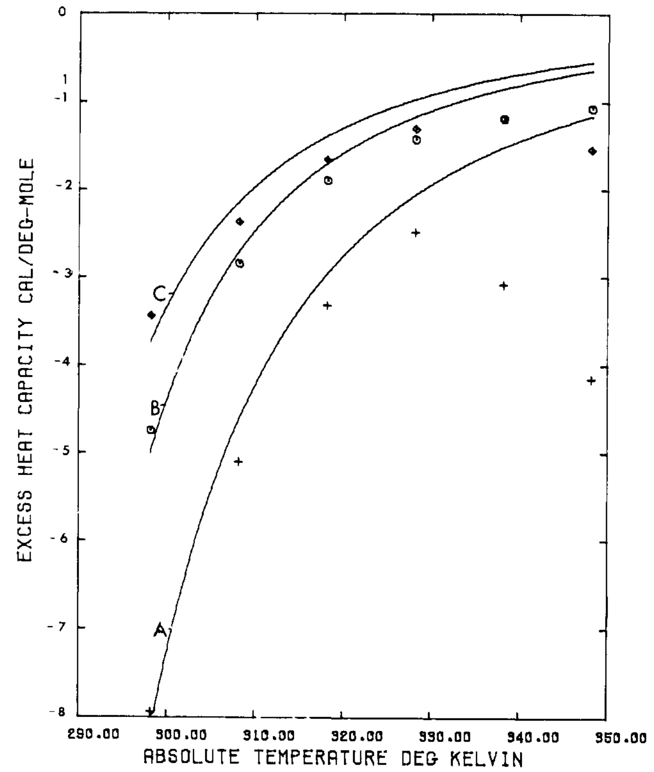

Figure 2. Excess heat capacities of mixing as a function of temperature for the same systems as in Figure 1. Here too the symbols correspond to the experimental values from ref 8b divided by $x_A x_B$. The solid curves are obtained from eq 36 using N^* and T^* from Table I: (A) n-C$_{16}$ in heptamethylnonane (+); (B) n-C$_{16}$ in squalane (⊙); (C) n-C$_{14}$ in squalene (◇).

It is hoped that the presentation of a theory of enhanced correlation in the n-alkanes might encourage efforts to resolve the experimental ambiguities.

Summary

A simple fluctuation theory of enhanced local orientational order in liquid n-alkanes is presented and shown to account well for recently observed thermal anomalies in mixtures of n-alkanes with globular, order-breaking solutes. Though the orientational pair correlations grow longer ranged with the approach to the freezing point, in the fashion of order parameter correlations in isotropic liquid crystals, the n-alkanes are much further from the pseudo-critical temperature T^*, and the correlation length is likely much shorter than in the liquid crystal systems.

The entropy of the order is predicted to be negative and to behave as $-(T - T^*)^{-1}$ with temperature. Possible anomalies in other properties near the freezing point are discussed. The magnetic birefringence and depolarized Rayleigh scattering intensity should increase with decreasing temperature as $(T - T^*)^{-1}$.

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(18) Professor P. Bothorel has informed the author that a study of the temperature dependence of the depolarized Rayleigh scattering from liquid alkanes and their mixtures is being undertaken in collaboration with P. Maelstaf. A determination of the temperature dependence of the integrated intensity would help support or refute the postulated temperature dependence of $w(p,2)$ in eq 28. From the angular dependence of the depolarized light scattering spectra, the correlation length of the fluctuations can be found. The model $w(p,2)$ of eq 28 predicts a correlation length ξ for the CSO which behaves as $\xi \sim [b/a(T - T^*)]^{0.5}$, just above the freezing point. G. Patterson has informed the author that the depolarized scattering intensity from the alkanes does get large just before freezing, possibly with the temperature dependence $(T - T^*)^{-1}$, but has expressed doubt that this could be attributed to the kind of order fluctuations proposed in this paper (private communication).

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(20) One reviewer expressed strong objections to (a) the idea that the orientational correlations in the n-alkanes are of a liquid-crystal character; and (b) the assumption that n-alkane liquids are about to undergo a critical, or near-critical, transition. Since the first is a fundamental assumption of the article, and the second is a sufficient (though not necessary) basis for eq 28, some reply is called for. (a) The basic characteristic of the liquid crystal state is long-range orientational order, in the absence of translational order in all three dimensions. To accomplish this ordering, the forces of anisotropy between the molecules must be capable of leading to intermolecular rotational barriers greater than kT in the liquid range of density and temperature. Anisotropy of shape appears to be a necessary property for the molecules to have. Liquid n-alkanes must be sufficiently long (greater than 10 carbons) before this is possible since the shape anisotropy of a single segment is not sufficient to bring about a nematic transition. Hydrocarbon chains are known to exist in a liquid crystal state in bilayer membranes (ref 19). Though the polar head group aids the establishment of order by restricting translational freedom, the chains must maintain the order by virtue of the intermolecular potential and must do so in the face of a large degree of lateral mobility. The rate of lateral diffusion of a lipid molecule in a biological membrane is comparable to translational diffusion rates in a normal liquid (see, for instance, G. Vanderkooi, *Biochim. Biophys. Acta,* **344,** 307 (1974)). The view is here taken that the orientational order of hydrocarbon chains in membrane bilayers is a result of the normal forces of anistropy between them, and not brought about by any fundamental modification of the intersegment potential by either the polar head group or the presence of the interface. (b) The nematic-isotropic transition is *not* a critical transition in practice, nor is it expected to be on theoretical grounds (ref 11, p 48). The motivation for De Gennes' use of the Landau expansion was the weak first-order nature of the transition which suggested that the free energy densities of the ordered and disordered phases were not too different. On these grounds, order fluctuations from the isotropic to the anisotropic state could occur which were not especially costly in free energy. T^* was the temperature, below the actual transition temperature, at which the free energy densities of the ordered and disordered phases would vanish if order and density were not coupled. At the actual transition, the system undergoes finite volume change. The orientational and radial components of the pair correlations are coupled and "spoil" the pure rotational transition. It is thought that the bulk of the energy jump at the transition is due to the volume change. Why then does a theory of critical fluctuations work so well near a transition which is not, and cannot be, a critical one? Not only does the theory work well, it works too well. The first power $(T - T^*)$ dependence of the counterpart of $w(p,2)$ in eq 28 in the text is obeyed right up to the nematic transition, while this is not at all the case for real critical systems (see ref 11, p 48–50). A smiliar situation happens for the superconducting transition, and De Gennes offers the possible explanation that the length/width ratio is large enough so that the classical theory of critical points works. If the classical theory of critical fluctuations is approximately valid for systems in which there is a large length parameter (even though the incipient order–disorder transition is not critical), then might it not succeed for long n-alkanes? The determining factor is not the strength of the first-order transition which occurs before T^* is reached, since this may reflect coupling effects of the density to the order, but rather the difference in free energy between ordered and disordered regions of fluid at *constant volume.* Finally, just as for liquid crystal and superconducting transitions, one need not be "close" to a critical point or pseudo-critical point to sense fluctuations from the mean-field or random phase behavior of the system. The data may be from the wings of the critical region. In the case of isotropic liquid crystals it is possible to measure scattering from the order fluctuations 60–70 °C above T^*. Certainly the fluid is not close to the transition, yet the fluctuations are measurable.

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