

On the opposite, in Maier-Saupe's analysis, steric effects are neglected :

$$\Sigma_1 = 0.$$

The relative weight x of Σ_1 in $g(P, T)$ for the case of PAA can be estimated from the latent heat at the transition :

$$\Delta H = T\Delta\Sigma = T \frac{\partial(\mu_N - \mu_I)}{\partial T} = \frac{1}{2} S_c^2 g_c \left(1 - \underbrace{\frac{T_c}{g_c} \left(\frac{\partial g}{\partial T} \right)_c}_x \right).$$

Clearly, x is a measure of the entropic contribution to the couplings :

for hard rods, $g = T\Sigma_1(S)$ whence $\partial g/\partial T = g/T$ and $x = 1$; for Maier and Saupe, g is independent of T (at constant volume) and $x = 0$.

The actual value of x is :

$$x = 1 - \frac{2\Delta H}{S_c^2 g_c} = 1 - \frac{2\Delta H}{4.54 S_c^2 T_c}.$$

Unfortunately, the dispersion of the existing data on ΔH (or alternatively dT_c/dP) does not permit a precise determination of x . Taking the data on ΔH ⁽¹⁴⁾, and a value of S coherent with the theoretical calculation of $(T/g)_c \cdot ((T/g)_c = 4.54, S_c = 0.43)$, we get :

$$x \simeq 0.5.$$

This suggests that the contributions of Van der Waals attractions and entropic repulsions (excluded volume effects) to the intermolecular orientational couplings $\frac{1}{2}g(P, T)S^2$ are on the same order of magnitude.

5. Conclusions

(a) Experimentally S_c is independent of P on a rather broad range of pressure.

(b) This is compatible with all mean field models where the molecular interaction energy is proportional to S^2 ; thus our experiment does not give a very detailed check on the nature of the couplings. They might be temperature independent, as in Maier-Saupe's theory (Van der Waals attractions), or temperature dependent, as in the Onsager's calculation (excluded volume effects). In

fact, we probably have a superposition of both effects; the relative weights of the two contributions can be estimated by certain other measurements, such as the latent heat of the transition. A rough estimate along these lines shows that the two effects are on the same order of magnitude.

(c) We are unable to devise a similar theory for the solid-nematic transition, because the order parameter for this transition is more complex: it depends on S , but also on the translational order of the molecules.

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