where P is the probability for one molecule to have its orientation in the solid angle $\mathrm{d}\Omega$.

To compute Σ_0 explicitly, we make a molecular field approximation on the distribution P. This amounts to taking:

$$P(\theta) = \text{const. } \exp \lambda\left(\frac{3\cos^2\theta - 1}{2}\right)$$

where the const. ensures $\int P\,\mathrm{d}\Omega = 1$, and λ is defined implicitly in terms of S by the condition:

$$\int P\,\mathrm{d}\Omega\,\frac{3\cos^2\theta - 1}{2} = S.$$

In such an approximation, the probabilities P (and therefore also Σ_0) depend explicitly only on S.

The detailed resulting form for $\Sigma_0(S)$ can be extracted numerically from the work of Maier and Saupe.

Equation of state

We get the equation of state for the nematic phase by minimizing $\mu_N(P, T, S)$ with respect to S:

$$\frac{\partial \mu_N}{\partial S} = 0 \quad \text{whence} \quad S = \frac{T}{g(P, T)}\left|\frac{\partial \Sigma_0}{\partial S}\right|. \tag{1}$$

This is an implicit equation for S as a function of the single parameter $T/[g(P, T)]$. It may also be written explicitly:

$$S = f\left(\frac{T}{g(P, T)}\right). \tag{2}$$

The general behaviour of S expected from such an equation of state is shown in Fig. 4.

Now it is clear that the equilibrium value of S in a certain state (P, T) of the nematic phase is fixed only by the value of the *reduced temperature* $T/g(P, T)$. In order words, if P and T vary along a line of constant T/g, the order parameter will be constant.

This is especially true at the nematic–isotropic transition; the chemical potentials of both phases are then equal:

$$\mu_N = \mu_I \quad \text{whence} \quad S_c^2 = \frac{T_c}{g(P_c, T_c)}\,\Sigma_0(S_c). \tag{3}$$

Equations (2) and (3) define completely the values of S and T/g at the transition: whatever the pressure, the transition always occurs

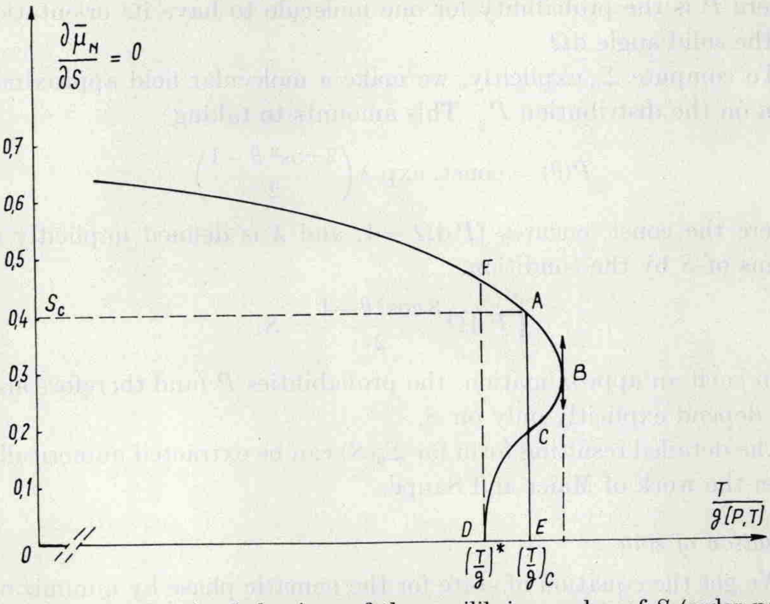

Figure 4. Qualitative behaviour of the equilibrium value of S (order parameter of the nematic phase) *versus* reduced temperature $T/g(P,T)$. Points A, B, C, D, E, F have the same meaning as in Fig. 3.

for the same values $S = S_c$ and $T/g = (T/g)_c$. From Maier–Saupe's analysis (i.e. from their computation of Σ_0) we know that: $S_c = 0.43$ and $(T/g)_c = 4.54$ *independently of the detailed form of* $g(P, T)$.

The knowledge of $g(P,T)$ would give (from Eqs. (2) and (3)) the dependence of the transition temperature versus pressure. Alternatively, we could use the measured $\mathrm{d}T_c/\mathrm{d}P$ to check a theoretical guess of $g(P,T)$. In particular, it would be interesting to know whether g is dominated by Van der Waals attractions or by steric repulsions. This can be attempted by the following arguments:

The total entropy Σ of the nematic phase can be divided into 2 parts:

—the "one molecule orientational entropy" Σ_0

—the entropy Σ_1 associated with the interactions of molecules of different orientations (excluded volume effects): this is the entropic part of the coupling free energy $\frac{1}{2}S^2g(P,T)$.

For example, in the hard rod gas, g is purely entropic:

$$\tfrac{1}{2}S^2g(P,T) = T\Sigma_1.$$