

Figure 2. Nematic phase order parameter *versus* pressure, at the solid nematic (dots) and nematic-isotropic (triangles) transitions. The volume change associated with our maximal pressure (3 kbar) is about 15%, and the corresponding variation of the absolute temperature of the transition is 17%.

dependence on  $S$  of the various terms, and then make a list of the different assumptions implicated by this expression:

$$\mu_N(P, T, S) = \mu_I(P, T) - \frac{1}{2}g(P, T)S^2 - T\Sigma_0(S).$$

A qualitative picture of the variation of  $\mu_N$  with  $S$  close to the transition is shown in Fig. 3.

4.1.  $\mu_I(P, T)$  is the part of  $\mu_N$  which is independent of the long range order  $S$ ; it can be considered as the chemical potential of the isotropic phase at the same  $P$  and  $T$ .<sup>(25)</sup>

4.2. Coupling free energy  $\frac{1}{2}S^2g(P, T)$ . This is the free energy

corresponding to the interactions between molecules of different orientations. It will contain two contributions:

- ( $\alpha$ ) Van der Waals attractions.
- ( $\beta$ ) Steric repulsions.

The contribution from ( $\alpha$ ) is expected to be roughly proportional to  $1/V^{2(18)}$  and independent of  $T$  (at constant volume). The contribution from ( $\beta$ ) was disregarded by Maier and Saupe, but might well be important; it has been discussed by Onsager for the very special case of hard rods<sup>(26)</sup>: in such a case it is linear in  $T$ . The volume dependence of ( $\beta$ ) for a dense nematic is not known (the Onsager analysis applies only for dilute rods).<sup>(27)</sup>

Here our main assumption is that both contributions ( $\alpha$ ) and ( $\beta$ ) can be approximated by a term  $-\frac{1}{2}g(P, T)S^2$  quadratic in the order parameter. The limits of validity of this assumption are unclear (in the Onsager model this approximation would be in fact rather poor), but it leads to values of  $S_c$  which are quite reasonable ( $S_c \sim 0.43$ )<sup>(28)</sup>.

4.3. Orientational entropy  $\Sigma_0$ . This is the orientational entropy for one molecule. It is defined by:

$$\Sigma_0 = - \int P \log P \, d\Omega$$

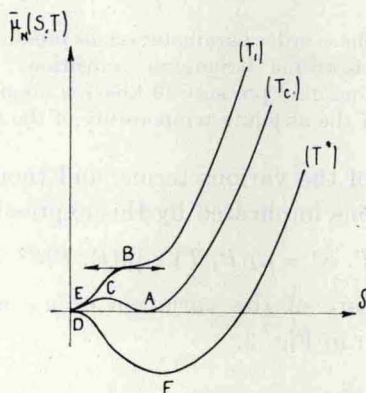


Figure 3. Chemical potential  $\bar{\mu}_N(S, T/g)$  versus order parameter  $S$  at various temperatures close to the nematic-isotropic transition. Points  $E$  and  $A$  correspond to the actual transition,  $D$  is the supercooling limit of the isotropic phase, and  $B$  the (hypothetical) limit of superheating of the nematic phase: the system converts from  $A$  to  $E$  or *vice versa* before points  $B$  or  $D$  are actually reached.