

wave modulation model—which corresponds to $n_c \rightarrow 0$ —is thus here a good approximation for a large part of the I phase.

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Tricritical Points in the Equilibrium Polymerization of Sulfur Solutions

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A dilute $n \rightarrow 0$ vector model provides a useful description of equilibrium polymerization in a solvent. Such polymerization occurs in liquid sulfur solutions and leads to a lower critical solution point that is analogous to the tricritical point found in ^3He - ^4He mixtures. In the mean-field approximation, the model is identical to an earlier theory of Scott. Nonclassical critical behavior can explain certain discrepancies between Scott's theory and experiment.

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Recently we have shown^{1,2} that equilibrium polymerization can be described by the $n \rightarrow 0$ limit of the n -vector model of magnetism in a small magnetic field, and that evidence for the nonclassical critical behavior of the $n \rightarrow 0$ vector model can be seen in the polymerization of liquid sulfur. In the molecular-field approximation, the $n \rightarrow 0$ vector model becomes identical² with the Tobolsky-Eisenberg³ theory of equilibrium polymerization.

Solutions of liquid sulfur with a variety of organic solvents are unusual⁴⁻⁶ in that they exhibit

a temperature range of complete miscibility of the components, bounded below by the familiar upper critical solution temperature (UCST), T_1 , and low-temperature phase separation, and bounded above by a lower critical solution temperature (LCST), T_2 , above which the components again undergo phase separation. Scott⁴ has presented a theory of these solutions based on the Flory-Huggins⁷ theory of polymers and the Tobolsky-Eisenberg³ theory of polymerization, and has shown that it is capable of reproducing many of the quali-

tative features found⁶ in these solutions.

In this Letter we introduce a dilute n -vector model that, in the $n \rightarrow 0$ limit, provides a useful model of equilibrium polymerization in a solvent and, in particular, of the polymerization and phase equilibria of liquid sulfur solutions with various organic solvents.⁴⁻⁶ In the molecular-field approximation this model becomes identical with Scott's theory. Through the correspondence with the dilute $n \rightarrow 0$ vector model, the UCST in sulfur solutions is seen to be an ordinary critical point governed by Ising exponents whereas the

LCST is found to be intimately related to the *tri-critical points* found in models of dilute ferromagnets and ³He-⁴He solutions. The phase diagrams for sulfur solutions in an appropriate variable space are intimately related to those of the Blume-Emery-Griffiths⁸ (BEG) model of ³He-⁴He mixtures. In this Letter we define our model and outline some of the results. The details of the calculations and the resulting phase diagrams will be presented elsewhere.⁹

Consider first the dilute n -vector model with Hamiltonian

$$\mathcal{H} = -K \sum_{\langle i, j \rangle} \nu_i \nu_j - \Delta \sum_i \nu_i - J \sum_{\langle i, j \rangle} \nu_i \nu_j \vec{S}_i \cdot \vec{S}_j - m_0 H \sum_i \nu_i S_i^{(1)}, \quad (1)$$

where the sum \sum_i extends over all sites and $\sum_{\langle i, j \rangle}$ extends over all distinct nearest-neighbor pairs of lattice sites, where ν_i is a spin- $\frac{1}{2}$ variable ($\nu_i = 0, 1$) with $\nu_i = 1$ corresponding to a magnetic spin \vec{S} occupying site i and $\nu_i = 0$ corresponding to a nonmagnetic impurity, and where \vec{S} is a classical n -component vector "spin" of length \sqrt{n} and $S^{(1)}$ is its component parallel to the field H . In the limit $n \rightarrow 0$ the partition function of this model can be written in the form¹⁰

$$Z = e^{Nf} = \text{Tr} e^{-\mathcal{H}/k\tilde{T}} = \sum_{\{\nu_i\}} \exp(\tilde{K} \sum_{\langle i, j \rangle} \nu_i \nu_j + \tilde{\Delta} \sum_i \nu_i) \sum_{N_p} \sum_{N_b} \sum_{N_1} (\tilde{J})^{N_b} (h^2)^{N_p} (\frac{1}{2})^{N_1} \Gamma(N_p, N_b, N_1, N; \{\nu_i\}), \quad (2)$$

where $\tilde{K} = K/k\tilde{T}$, $\tilde{\Delta} = \Delta/k\tilde{T}$, $\tilde{J} = J/k\tilde{T}$, and $h = m_0 H/k\tilde{T}$, with \tilde{T} the temperature of the magnetic model, where $\sum_{\{\nu_i\}}$ is the sum over all assignments of $\nu_i = 0$ or 1 to each site, and where $\Gamma(N_p, N_b, N_1, N; \{\nu_i\})$ is the number of ways of placing N_p self-avoiding and mutually avoiding walks containing exactly N_b bonds on the lattice of N sites such that there are exactly N_1 single-site, no-bond walks and such that every site visited by any walk has $\nu_i = 1$. Although the sum in (2) contains single-site walks, it contains no closed loops.

Now consider the following model for equilibrium polymerization in a solvent. Each site can be occupied by either a solvent molecule (denoted by subscript 0), or by a S_8 (monomer) unit (denoted by subscript s), which may be either a closed ring or open as part of a polymer (possibly of length 1). There are nearest-neighbor interaction energies between solvent and monomer molecules given by E_{00} , E_{0s} , and E_{ss} for solvent-solvent pairs, etc. In addition to the Boltzmann factors arising from these interactions, the statistical weight of any given linear polymer consisting of m monomers [and therefore $(m-1)$ bonds] with a specific embedding on the lattice is taken to be K_1 if $m=1$, and $2K_1(K_p')^{m-1}$ if $m>1$, where

$$\begin{aligned} K_1 &= \exp[(T\Delta S_1 - \Delta H_1)/kT], \\ K_p' &= \exp[(T\Delta S_p' - \Delta H_p)/kT]. \end{aligned} \quad (3)$$

The statistical weight of any closed-ring polymer

containing more than one monomer is taken to be identically zero. The detailed motivation for this choice is presented in Ref. 9. Here we merely note that $\Delta S_p'$ and K_p' do not contain contributions from the number of ways to arrange the polymer on the lattice and are distinct from ΔS_p and K_p of Scott's theory. With the identifications

$$\begin{aligned} \tilde{J} &= K_p', \quad \tilde{K} = (2E_{0s} - E_{00} - E_{ss})/kT, \\ \frac{1}{2}h^2 &= K_1, \quad \tilde{\Delta} = [\mu_s - \mu_0 + q(E_{0s} - E_{00})]/kT, \end{aligned} \quad (4)$$

where μ_s and μ_0 are chemical potentials of S_8 (monomer) units and solvent, respectively, the ("semigrand") partition function appropriate to this sulfur solution, Y , is given in terms of Z in Eq. (2) by

$$Y = \exp(\frac{1}{2}qNE_{00}/kT) Z(\tilde{K}, \tilde{J}, h, \tilde{\Delta}, N), \quad (5)$$

where q is the coordination number of the underlying lattice ($q=6$ for simple cubic).

For the polymer solution the volume fraction of sulfur, φ_s , the volume fraction of polymer, φ_μ , the volume fraction of unpolymerized sulfur, φ_λ , and the average number of monomers per polymer, P , are given in terms of the magnetic variables by

$$\begin{aligned} \varphi_s &= x_s, \quad \varphi_\mu = \tilde{J}e + \frac{1}{2}hm, \\ \varphi_\lambda &= \varphi_s - \varphi_\mu, \quad P = 1 + \frac{2\tilde{J}e}{hm}, \end{aligned} \quad (6)$$

where $m = \partial f / \partial h$, $e = \partial f / \partial \tilde{J}$, and $x_s = \partial f / \partial \tilde{\Delta}$.

The molecular-field approximation to our dilute $n \rightarrow 0$ vector model can be obtained by following the procedure used by Blume, Emery, and Griffiths⁸ to treat the corresponding $n = 1$ case with the appropriate change of definition of trace, and treatment of the $n \rightarrow 0$ limit.¹¹ This calculation is given in detail elsewhere.⁹ The results can be summarized by the equations

$$\begin{aligned} f(\tilde{K}, \tilde{J}, \tilde{\Delta}, h) &= -\frac{1}{2}q\tilde{K}x_s^2 - \frac{1}{2}q\tilde{J}m^2 - \ln(1-x_s), \\ (1-x_s)^{-1} &= 1 + [1 + \frac{1}{2}(q\tilde{J}m+h)^2] \exp(\tilde{\Delta} + q\tilde{K}x_s), \quad (7) \\ m &= (1-x_s)(q\tilde{J}m+h) \exp(\tilde{\Delta} + q\tilde{K}x_s), \quad e = \frac{1}{2}qm^2. \end{aligned}$$

Under an appropriate identification of variables this result becomes *identical* with Scott's theory⁴ of polymer solutions. The connection is given by the equations (derived in Ref. 9)

$$\begin{aligned} K_1 &= \frac{1}{2}h^2, \quad K_p = q\tilde{J}, \quad \frac{2w}{RT} = q\tilde{K}, \\ \ln a_0 &= -f, \quad \ln \frac{a_\lambda}{a_0} = \tilde{\Delta}, \quad (8) \\ \varphi_\lambda &= \frac{1}{2}x_s \{1 \pm [1 - 2(m/x_s)^2]^{1/2}\}, \quad \varphi_\mu = x_s - \varphi_\lambda, \end{aligned}$$

where K_p is Scott's propagation equilibrium constant, w is his interaction parameter, a_0 and a_λ are the activities of solvent and sulfur, respectively, and where the plus sign is appropriate when $|h| < \sqrt{2}(1 - q\tilde{J}x_s)$.

The connection between the phase diagrams found by Scott for sulfur solutions and those appropriate to dilute magnetic models⁸ is clarified by examining the $h = 0$ phase diagram of our $n \rightarrow 0$ vector model in $(\tilde{J}, \tilde{K}, \tilde{\Delta})$ space. Figure 1 shows the projection of several important features in this diagram into $(q\tilde{J}, q\tilde{K})$ plane. Curve c is the line of critical points bounding the phase separation between spin-rich and solvent-rich nonmagnetized phases, driven by the interaction K . It occurs at $q\tilde{K} = 4$, independently of $q\tilde{J}$, and ends in a critical end point at $q\tilde{J} = 1.502$. Curve t is the tricritical line along which the critical surface for magnetic ordering (critical polymerization surface), $q\tilde{J}x_s = 1$, becomes a first-order transition surface. It is the locus of LCST's, T_2 . Curve e is the critical end-point line at which the critical surface for magnetic ordering meets the coexistence surface for the separation of nonmagnetic phases. Curves e and t meet at the tricritical end point ($q\tilde{K} = 4.513$, $q\tilde{J} = 1.285$). The dashed line between this tricritical end point and the critical end point of curve c is a line of three-phase equilibrium between two nonmagnetized phases

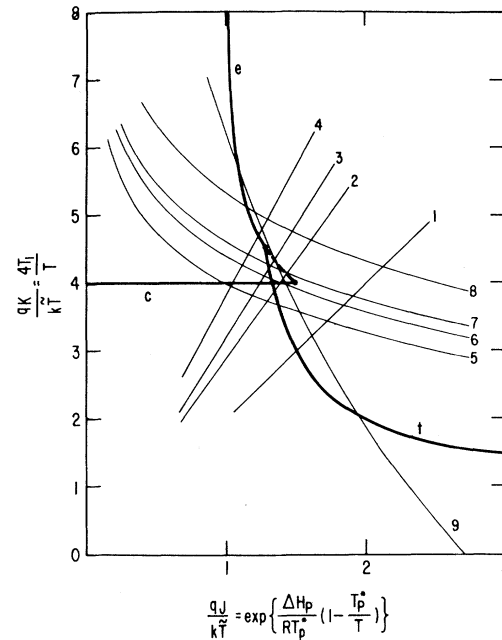


FIG. 1. Phase diagram in field space for the dilute $n \rightarrow 0$ vector model in the molecular-field approximation. The figure shows the projection along the $\tilde{\Delta}$ axis into the $(q\tilde{J}, q\tilde{K})$ plane of the important features of the $h = 0$ phase diagram. See text for details.

and the magnetically ordered phase.

The relationship between the phase diagrams of Scott's theory and those for dilute magnets can be seen by comparing the light lines numbered 1-9 in Fig. 1. Lines 1-4 are straight lines through the origin corresponding to various choices of K/J in the $n \rightarrow 0$ vector model. They give phase diagrams similar (although not, of course, identical) to those in Figs. 5(b)-5(d) of Blume, Emery, and Griffiths.⁸ (Their model is equivalent to a dilute spin- $\frac{1}{2}$ Ising model, and is identical with our dilute n -vector model with $n = 1$. The molecular-field approximation to our model with $n = 1$ reproduces the BEG theory exactly.) The curves appropriate to sulfur solutions are obtained by setting

$$q\tilde{J} = K_p(T)/K_p(T_p^*), \quad q\tilde{K} = 4T_1/T, \quad (9)$$

where $T_p^* = 432$ K is the polymerization temperature of pure sulfur and T_1 is the critical temperature of the low- T separation. Curves 5-8 are appropriate to sulfur solutions and give phase diagrams identical to those in Figs. 6(a), 6(b), 7(b), and 8(b), respectively, of Scott.⁴

An advantage of the phase diagram shown here is that new types of phase diagrams are easily

anticipated. For example, with other choices of $\Delta H_p/RT_p^*$ than that appropriate for sulfur, a new type of phase diagram is possible, unlike any of those found by Scott. This is illustrated by curve 9, which corresponds to $\Delta H_p/kT_p^*=1.0$ and $T_1/T_p^*=1.55$. [The shape of the corresponding phase diagram in the (T, x) plane is left as an exercise to the reader, and will be given in Ref. 9.]

The nonclassical critical behavior to be expected for this dilute $n \rightarrow 0$ vector model should help to resolve certain discrepancies between the mean-field predictions of Scott's theory and the experimental phase diagrams for sulfur solutions. In the limit $K_1 \rightarrow 0$ the mean-field theory coexistence curve is "pointed" at T_2 with the composition difference between coexisting phases vanishing linearly with $T - T_2$, and the critical polymerization line passing smoothly into the unpolymerized branch of the coexistence curve in the (T, x) plane. In contrast, the experimental curves⁶ for sulfur solutions are rounded, apparently becoming horizontal at T_2 , and the polymerization curve does not appear to be a simple extension of the unpolymerized branch. While the nonzero value of K_1 will produce some rounding of the coexistence curve, the accepted values of K_1 are too small to produce the observed rounding ($K_1 \sim 10^{-10}$ at T_2 , and the resulting shift of T_2 is about 1 °K).

Simple scaling equations of state¹² are capable of producing a break in slope between the critical curve and the coexistence curve, and renormalization-group studies^{13, 14} indicate logarithmic corrections to mean-field theory that result in rounding of the coexistence curve to a shape that is asymptotically flat at T_2 . These logarithmic corrections are difficult to detect in ³He-⁴He mixtures¹⁵ and vanish¹⁶ in the limit $n \rightarrow \infty$. Theoretical estimates¹⁴ and Monte Carlo calculations¹⁷ indicate that such corrections may be important for $n=1$, however, and an estimate along the lines of Ref. 14 indicates that they will be even more important as $n \rightarrow 0$. The possibility that logarithmic corrections to tricritical phenomena might be observed by examining sulfur solutions is an exciting prospect.

Another modification of Scott's predictions occurs at the critical end point on curve 8 in our figure and in Fig. 8(b) of Scott.⁴ According to mean-field theory, the phase boundary of the sulfur-rich phase undergoes a simple discontinuity of slope at the polymerization line in the $K_1 \rightarrow 0$ limit. According to our model, the slope dx_s/dT of this phase boundary should remain finite as

the critical polymerization line is approached from below, but should diverge as it is approached from above (in the $K_1 \rightarrow 0$ limit):

$$\frac{dx_s}{dT} \sim \begin{cases} \text{const}, & T \leq T^* \\ (T - T^*)^{-\alpha}, & T \geq T^* \end{cases}, \quad (10)$$

where $\alpha = 0.24$ according to recent estimates.¹⁸ This prediction seems in somewhat better agreement than mean-field theory with the phase diagram observed for sulfur with *trans*-decaline^{5, 6} and carbon tetrachloride.⁶

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