will no longer be equal to each other nor can they be expressed simply in terms of these orbit elements. Fortunately in the case of the binary pulsar the time scale for these changes is of the order of ϵ^{-5} times the period of the system. As a consequence one can make use of the method of multiple time scales to evaluate these integrals.

In this method one assumes that the orbit elements are functions of a "slow" time $\epsilon^5 t$ while the other motion variables are functions of a "fast" time t. In lowest order of approximation one can then neglect the slow-time variation of the orbit elements in evaluating the integrals over Σ_1 and Σ_2. The result is that they are again in lowest order of approximation equal to the Newtonian expressions for the energy and angular momentum of the system. They differ slightly in value from each other, however, because the orbit elements appearing in these expressions have slightly different values on Σ_1 and Σ_2. The difference between the two integrals can therefore be expressed in terms of the rates of change of the orbit elements and these in turn can be related to the integrals over S in the balance equations (3) and (4). In this way one obtains expressions for the rates of change of the semimajor axis and eccentricity of the Newtonian orbits that are equal to the expressions (5.6) and 5.7) given by Peters and used by Taylor in the analysis of his observations.

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Equilibrium Polymerization as a Critical Phenomenon

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Equilibrium polymerization can be described by the $n \to 0$ limit of the n-vector model of magnetism in a small magnetic field. Nonclassical critical effects are predicted. The earlier theory of Tobolsky and Eisenberg is a mean-field approximation to the present theory. An application is made to the polymerization in sulfur.

A great variety of organic and inorganic compounds can polymerize to form linear and nonlinear polymers.[1] In many cases, polymerization proceeds under conditions of equilibrium between monomer and polymer,[2] and interesting transition phenomena can occur.[3]

One of the oldest and most studied examples of equilibrium polymerization showing a well-defined transition is the polymerization of liquid sulfur.[4] Sulfur melts at 115 °C to give a mobile yellow liquid consisting primarily of S_8 rings. Above about $T_c = 159$ °C these rings polymerize to form long chains, and the liquid becomes brown in color and extremely viscous. The abruptness of the onset of polymerization at 159 °C results in anomalies in physical properties of sulfur reminiscent of a second-order or λ transition. The specific heat exhibits an abrupt rise close to T_c and then decreases less rapidly for $T > T_c$. The weight fraction of polymer, which is nearly zero below T_c, increases rapidly for $T > T_c$. There is a dramatic rise in the viscosity and average molecular weight within a few degrees of T_c.

The polymerization transition in liquid sulfur was first treated by Gee,[5] who used distinct descriptions above and below T_c. The first unified theory, due to Tobolsky and Eisenberg,[6] is based on chemical equilibrium theory with only two equilibrium constants, $K_1 = \exp[(T\Delta S_1 - \Delta H_1)/RT]$ and $K_P = \exp[(T\Delta S_P - \Delta H_P)/RT]$, where K_1 describes the initiation of the polymerization through opening of S_8 rings and K_P describes the propagation reaction. If c_{00} is the initial concentration of S_8 rings and c_0 the concentration of S_8 rings at equilibrium, then the concentration of polymers, c_p, and the concentration of monomers incorporated in polymers, c_m, are given in the Tobolsky-Eisenberg (TE) theory by

$$c_p = K_1 c_0/(1 - K_P c_0),$$
$$c_m = K_1 c_0/(1 - K_P c_0)^2, \qquad (1)$$

where c_0 satisfies the "equation of state"

$$c_0 + c_m = c_0 + K_1 c_0/(1 - K_P c_0)^2 = c_{00}. \qquad (2)$$

If $K_1(T_c) \ll 1$ the system exhibits a "transition." At low temperatures c_m and c_p are very small and $c_0 \approx c_{00}$. As K_P passes through $K_P{}^c = c_{00}{}^{-1}$, the quantities c_m and c_p abruptly start to increase; the system polymerizes. The number average chain length, $P = c_m/c_p$, rises to a maximum value $P_{max} \sim K_1{}^{-1/2} \sim 10^5\text{--}10^6$. The sharpness of the transition depends upon the smallness of $K_1(T_c)$. Only in the limit $K_1(T_c) \to 0$ does the transition become mathematically sharp. For sulfur, $K_1(T_c) \sim 10^{-12}$ so the transition is very sharp and critical effects are to be expected, as argued below.

In this Letter we present for the first time a direct theoretical contact between equilibrium polymerization and the theory of phase transitions and critical phenomena.[7] Equilibrium polymerization can be described by the $n \to 0$ limit of the n-vector model of magnetism in the presence of a very small magnetic field H. The resulting model exhibits critical behavior characterized by nonclassical critical exponents. Tobolsky and Eisenberg's theory is shown to be a mean-field approximation to the model. The $n \to 0$ vector model has been used previously[8,9] to describe the statistics of long polymers in solution, but that analogy suffers from a difficulty in treating polydispersion.[10] In the case of equilibrium polymerization, polydispersion effects are treated correctly.

Following Sarma,[11] consider the n-vector model on a $d = 3$ dimensional lattice of volume V with Hamiltonian

$$H = -J \sum_{\langle i,j \rangle} \vec{S}_i \cdot \vec{S}_j - \mu_0 H \sum_i S_i{}^{(1)}, \qquad (3)$$

where the sum $\sum_{\langle i,j \rangle}$ extends over all distinct nearest neighbor pairs $\langle i,j \rangle$ of spins, and where $\vec{S}$ is a classical vector of norm

$$|\vec{S}|^2 = \sum_{\alpha=1}^{n} [S^{(\alpha)}]^2 = n$$

and $S^{(1)}$ is its component parallel to the field H. In the limit $n \to 0$ the partition function Z and thermodynamic potential f for this model can be written[11]

$$Z = e^{+Vf} = \sum_{N_b N_P} (\tilde{\beta})^{N_b} (h^2)^{N_P} \Gamma(N_b, N_P, V), \qquad (4)$$

where $\tilde{\beta} = J/k\tilde{T}$ and $h = \mu_0 H/k\tilde{T}$, with $\tilde{T}$ the temperature of the reference n-vector model, and where $\Gamma(N_b, N_P, V)$ is the number of ways to put N_P self-avoiding and mutually avoiding walks (linear polymers with excluded volume) containing a total of N_b steps or bonds (bonds between monomers) on a lattice of V/v_0 sites, with v_0 the volume per site. The sum includes single-site walks with no bonds but excludes closed loops. If we make the correspondence

$$\tilde{\beta} = K_P \lambda^{-1}, \quad h^2 = K_1, \qquad (5)$$

where λ is an appropriate constant,[12] then Eq. (4) represents the partition function of a system of S_8 rings in equilibrium with polymers. Each lattice site contains an S_8 "monomer," either closed or open. Each term in Eq. (4) consists of a set of self-avoiding and mutually avoiding walks. A walk containing x bonds corresponds to a polymer containing $x + 1$ monomers, and is weighted by a factor K_1 for initial ring opening and by a factor $(K_P \lambda^{-1})^x$ for the x chain propagation steps. The

"unoccupied" sites in each term of Eq. (4) contain closed S_8 rings which act as a solvent for the polymer. We shall suppose that S_8 rings act like a good solvent, leading to an effective repulsion between open S_8 monomers. The concentrations c_m and c_p defined above are related to the magnetization density $m = \partial f/\partial h$ and the configurational energy density $e = \partial f/\partial \tilde\beta$ through the equations

$$c_p = \tfrac{1}{2}mh,$$
$$c_m - c_p = \tilde\beta e. \tag{6}$$

The equation of state $G(m, h, \tilde\beta) = 0$ of the $n \to 0$ vector model is needed to know how c_p, c_m, and $P = c_m/c_p$ vary as functions of T [through K_P and K_1 by use of Eq. (5)]. Here we shall assume that the $n \to 0$ vector model obeys scaling[13] when $\tilde\beta \to \tilde\beta_c$ and $h \to 0$, and we shall use for simplicity a linear parametric model[14] and neglect at this stage terms due to Goldstone modes when the coexistence curve is approached. The parametric representation is

$$K_1^{1/2} = h = ar^\Delta\theta(1 - \theta^2),$$
$$1 - K_P(T)/K_P(T_c) = \tau = r(1 - b^2\theta^2),$$
$$2c_p/K_1^{1/2} = m = m_0 r^\beta\theta, \tag{7}$$
$$c_m - c_p = \tilde\beta e = \tilde\beta_c e_0 r^{(1-\alpha)}\theta^2.$$

From the Maxwell relation $\partial e/\partial h = \partial m/\partial \beta$ it follows that

$$b^2 = \beta(\delta - 3)/\gamma\alpha \quad \text{and} \quad \tilde\beta_c e_0 = \tfrac{1}{2}\gamma a m_0. \tag{8}$$

The exponents α, β, γ, δ, and $\Delta = \beta\delta$ are critical exponents, defined in Ref. 7. They satisfy the scaling relations $\alpha + 2\beta + \gamma = 2$ and $\beta(\delta - 1) = \gamma$.

The theory of Tobolsky and Eisenberg corresponds to a mean-field approximation. The equation of state [Eq. (2)] can be rewritten in terms of the phase transition variables in the vicinity of $K_P^c = K_P(T_c) = c_{00}^{-1}$:

$$(m/2c_{00})^3 + (m/2c_{00})\tau = h + \cdots, \tag{9}$$

where $\cdots$ indicates the presence of higher-order terms. This corresponds to the parametric representation (7) with the values $a = 1$, $m_0 = 2c_{00}$, $b^2 = 2$, and $\alpha = 0$, $\Delta = \tfrac{3}{2}$. To go beyond mean field, including critical effects, we use Eq. (7) with critical exponents determined from field-theoretic methods[15]: $\alpha = 0.236$, $\Delta = 1.46$.

The vanishing of e in Eq. (7) for $\theta = 0$ is required by the $n \to 0$ vector model. It results in very different behavior for sulfur above and below T_c. In addition, there is a very narrow range of temperatures about T_c in which the rounding

effects of the small field $h = \sqrt{K_1}$ are important. For sulfur this range is

$$\Delta T/T_c \approx (RT_c/\Delta H_P)K_1^{(1/2\Delta)} \approx 10^{-4} \tag{10}$$

or $\Delta T \approx 0.05$ °K, which is smaller than the resolution with which experiments have been performed to date.

The behavior of the number average chain length, $P = c_m/c_p = 1 + [r(1 - \theta^2)]^{-1}$, is very much like that predicted by Tobolsky and Eisenberg. It varies as τ^{-1} for $T < T_c$ and rises smoothly to a maximum value proportional to $K_1^{-1/2}$. We have used $a = 1$ and the values of ΔS_1 and ΔH_1 given by TE. Our curve for $P(T)$ is essentially identical with theirs.

The weight fraction of polymeric sulfur, $\Phi = c_m/c_{00}$, has been measured recently by Koh and Klement[16] and is reproduced in Fig. 1, along with results from the asymptotic scaling theory in Eq. (7) (solid curve) and from the TE theory (dashed curves). Our predictions are the following:

$$K_P < K_P^c: \quad \Phi \sim K_1(K_P^c - K_P)^{-(\gamma+1)},$$
$$K_P \approx K_P^c: \quad \Phi \sim K_1^{(1-\alpha)/2\Delta}, \tag{11}$$
$$K_P > K_P^c: \quad \Phi \sim (K_P - K_P^c)^{1-\alpha}.$$

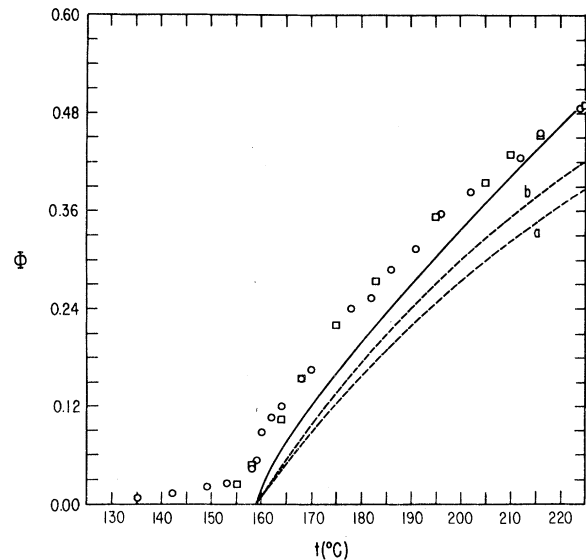Because K_1 is so small, Φ is essentially zero

FIG. 1. Weight fraction of polymeric sulfur. Squares and circles are the data of Koh and Klement (3 h, 60 min, respectively). Solid curve is the asymptotic theory from Eq. (7). Dashed curves give the TE theory with their original parameters (curve a) and with ΔH_P somewhat larger (curve b) corresponding to curve b in Fig. 2.

for $T < T_c$ and then increases with an exponent $1 - \alpha$. Thus, in the $K_1 \to 0$ limit, Φ rises linearly with T in the TE theory ($\alpha = 0$) but with infinite slope at T_c in the nonclassical theory. The latter prediction seems to be in better agreement with the data of Koh and Klement close to T_c. (Experimentally there is some insoluble sulfur even below T_c which is believed to be due to closed-ring polymers.)

The most striking predictions of the new theory occur for the specific heat. The singular part of the heat capacity (per mole of S_8), C_s, can be calculated from Eqs. (4)–(7) as

$$C_s = -\frac{\partial}{\partial T} \frac{\partial fv}{\partial (kT)^{-1}}$$

$$= \Delta H_P \frac{dc_m}{dT} + (\Delta H_1 - \Delta H_P)\frac{dc_p}{dT}. \tag{12}$$

The main theoretical prediction is the following:

$$K_P < K_P{}^c: \quad C_s \sim (\Delta H_P/RT)^2 K_1 \tau^{-2-\gamma},$$

$$K_P \approx K_P{}^c: \quad C_s \sim (\Delta H_P/RT)^2 K_1{}^{-(\alpha/2\Delta)}, \tag{13}$$

$$K_P > K_P{}^c: \quad C_s \sim (\Delta H_P/RT)^2 \tau^{-\alpha}.$$

For $T < T_c$ the small value of K_1 leads to $C_s \approx 0$ for both the TE and the present theory. At T_c there is a large enhancement due to critical fluctuations. Above T_c our curve falls more rapidly than that of TE. In Fig. 2 we present the data of West[17] for the heat capacity of liquid sulfur in the vicinity of the transition together with curves obtained from the asymptotic scaling theory in Eqs. (7) and (12) (solid curve) and from the TE theory (dashed curves). Corrections to scaling would be expected to become important when $\Delta \tau \gtrsim 0.01$ or $\Delta T \gtrsim 5°$, and addition of a correction to scaling improves the agreement with experiment away from T_c of the solid curves in both Figs. 1 and 2.

The nonclassical theory seems to be in better agreement with the large slope and curvature of West's data above T_c. However, it predicts a larger heat capacity spike than observed. This could be due to rounding by impurities or equilibration problems very close to T_c. More experimental data are needed in the immediate vicinity of the transition. Some more recent measurements[18] show higher peak values, a sharper spike, and lower values for $T < T_c$, all in agreement with our predictions. Clearly, however, further study of the equation of state of the n-vector model is also needed. The values of the remaining parameters used to produce Figs. 1 and 2 are $\Delta H_P/R$ = 1360 °K and $am_0 = 1.45 c_{00}$.
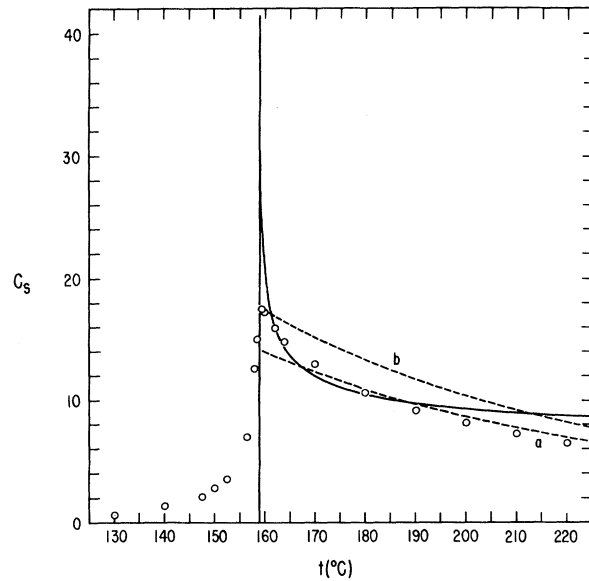

FIG. 2. Singular part of the heat capacity, per mole of S, in joules mole^{-1} K^{-1}. Circles are the data of West (a constant background, equal to the value at 120°C, has been subtracted), the solid curve is the asymptotic theory of Eqs. (7) and (12), and the dashed curves are the results of the TE theory with their original parameters (curve a), and with $\Delta H_P/R$ increased from 1595 to 1780°K to improve the heat capacity jump (curve b).

One limitation of the treatment given here that is shared by both the TE and Gee theories is that large closed rings are not accounted for. It has long been believed that the slow rise in heat capacity for $T < T_c$ and the small content of insoluble sulfur below T_c are due to these rings. It has been argued that these rings only contribute a few percent of the total sulfur. We have examined a generalization of TE theory which includes rings and find that it does produce a precurser in C, but does not significantly affect the predictions when $T > T_c$.

The details of the calculations leading to the results given here will be presented elsewhere. The same formalism can certainly be applied to many other systems exhibiting equilibrium polymerization.[19] Treatments of polymerization and phase transitions in liquid sulfur solutions and of copolymerization will be presented elsewhere.

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η Decay and the Quark Structure of the ε

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The decay rate for $\eta \to 3\pi$ is calculated with use of the u_3 tadpole piece of the quark Hamiltonian, but without assumptions of chiral perturbation theory. The calculation is performed within the framework of the bag model; however, the results are independent of bag parameters and depend only on (1) the light quark mass difference $|m_u - m_d|$ and (2) the quark structure of the $\epsilon(700)$. Comparison of the present calculated η decay rate with experiment shows that most theoretical estimates of $m_u - m_d$ imply a substantial four-quark component in the $\epsilon(700)$.

A convincing (and successful) calculation of the amplitude for $\eta \to 3\pi$ remains an elusive goal of the particle theorist. The problems associated with past calculations are well known,[1] and we sketch them briefly: Let $\mathcal{H}'$ be the Hamiltonian density responsible for the decay, and define the (dimensionless) Feynman amplitude

$$T(E_+, E_-, E_0) = \langle \pi^+ \pi^- \pi^0 | \mathcal{H}' | \eta \rangle, \tag{1}$$

where the pion energies E_+, E_-, and E_0 are defined in the c.m. system. In order to avoid the (experimentally *un*observed) Sutherland suppression[2] of the amplitude at $E_0 = 0$, it was proposed[3] to identify $\mathcal{H}'$ with the u_3 tadpole[4] associated with $\Delta I = \frac{1}{2}$ mass differences. In quark language,

$$\mathcal{H}' = (m_u - m_d)(\bar{u}u - \bar{d}d)/2, \tag{2}$$

where m_u and m_d are the current quark masses. With $\mathcal{H}'$ given by Eq. (2), one can show that T vanishes for $E_\pm = 0$ (i.e., $E_0 = m_\eta/2$), and hence

may be parametrized

$$T = A(1 - 2E_0/m_\eta), \tag{3}$$

which gives a good representation of the experimental Dalitz plot. It then remained to evaluate $A = T(m_\eta/2, m_\eta/2, 0)$; experimentally, $A = 0.65 \pm 0.13$.[5]

From this point, the calculational procedures become ambiguous. Contraction of Eq. (1) [using (2)] with all three pions soft brings one to an ill-defined point relative to the real Dalitz plot. The resulting amplitude is, in any case, small by a factor of $\sim\sqrt{3}$.[1] The case for chiral perturbation theory[6] in the square of the η four-momentum is also difficult to maintain in the face of possibly rapid momentum dependences of the matrix element due to Kogut-Susskind ghosts.[7]

In this paper we present a calculation of the amplitude A which circumvents the above problems. Although it is performed within the frame-