First-Order Transition in Doped Polyacetylene

Recently Kivelson and Heeger (KH)[1] have proposed that doped polyacetylene undergoes a first-order transition from a lattice of charged solitons into a polaron metal. In this Comment I show that thermodynamic consequences of this conjecture explain and tie together a variety of experimental data. The experiments considered are (a) a very sharp transition in the ESR response as function of the electrochemical potential μ,[2] (b) a plateau in the relation $\mu(\rho)$,[3] where ρ is the excess charge density on the polyacetylene chains (or the doping density), and (c) the diversity of data on the Pauli susceptibility χ_P for chemically doped samples.[2,4]

The KH conjecture is shown schematically in Fig. 1(a). The free energy is monotonic, but has a cusp at some density ρ_c where the free energies of two distinct configurations cross. KH propose that $\rho < \rho_c$ corresponds to charged solitons, while $\rho > \rho_c$ corresponds to polarons. The following reasoning, however, is independent of the detailed nature of the two configurations.

The form $F(\rho)$ in Fig. 1(a) implies that there are two densities ρ_1, ρ_2 connected by a line $F_{eq}(\rho)$ [the dashed line in Fig. 1(a)] with slope μ_c,

$$F_{eq}(\rho) = F(\rho_1) + \mu_c(\rho - \rho_1), \quad \rho_1 < \rho < \rho_2, \qquad (1)$$

such that the line is tangent to $F(\rho)$ at both ρ_1 and ρ_2. In terms of the chemical potential $\mu = \partial F/\partial\rho$ [Fig. 1(b)], $\mu_c = \mu(\rho_1) = \mu(\rho_2)$. Equation (1) is equivalent to the finding of a μ_c for which the Maxwell equal-area condition holds,

$$\int_{\rho_1}^{\rho_2} \mu(\rho)\, d\rho = \mu_c(\rho_1 - \rho_2). \qquad (2)$$

The meaning of this standard construction is phase separation: Divide the total volume V into volumes V_1, V_2 with densities ρ_1, ρ_2, respectively, such that $V = V_1 + V_2$ and $\rho V = \rho_1 V_1 + \rho_2 V_2$. The resulting free energy $[F(\rho_1)V_1 + F(\rho_2)V_2]/V$ is precisely Eq. (1), which is lower than the homogeneous $F(\rho)$ [Fig. 1(a)]. Thus for $\rho_1 < \rho < \rho_2$, the equilibrium situation is that of a two-phase system separated in space. It also follows that it is μ_c (and *not* ρ_c) which defines a proper first-order phase transition; at μ_c, the density jumps from ρ_1 to ρ_2.

It is interesting, however, that the KH conjecture implies $\partial\mu/\partial\rho > 0$, so that the homogeneous solution is locally stable. When this metastable situation is realized, it should exhibit hysteresis around ρ_c.

Phase separation in doped polyacetylene is unique since one phase has $\chi_P = 0$ (solitons), while the other phase has $\chi_P \neq 0$ (polarons). Thus $\chi_P(\mu)$ shows an abrupt jump at μ_c in agreement with recent data.[2] The plateau in $\mu(\rho)$ (Ref. 3) is also an obvious consequence [Fig. 1(b)].

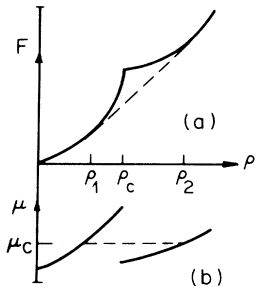

FIG. 1. (a) Schematic free energy for a homogeneous system (full lines) and a phase separated system (dashed line); (b) as in (a) for the chemical potential.

When ρ is fixed and $\rho_1 < \rho < \rho_2$, phase separation predicts that χ_P increases with the volume of the ρ_2 phase, i.e., $\chi_P(\rho) \sim \rho_2 V_2/V = \rho_2(\rho - \rho_1)/(\rho_2 - \rho_1)$. Phase separation also accounts for the presence of two types of spins.[4] It is possible, however, to achieve the homogeneous metastable phase with $\chi_P = 0$ for $\rho \lesssim \rho_c$. The latter situation is of considerable interest in view of its unusual relation with the conductivity.[1,2] Metastability thus accounts for the diversity of the $\chi_P(\rho)$ data.[2,4]

Data with Na doping[3] shows $\rho_1 \simeq 1\%$ and $\rho_2 \simeq 6\%$, which correlates well with the large jump in $\chi_P(\mu)$.[2] Similar data on other dopants and a reanalysis of $\chi_P(\rho)$ data should establish the important values of ρ_1, ρ_2. The transition is driven by on-chain interactions to the extent that ρ_1, ρ_2 are dopant independent.

Finally, it should be noticed that the microscopic origin of the KH conjecture and the nature of the polaron metal are not conclusive.[1] On the other hand, the KH conjecture does account, as shown here, for a large variety of experimental data.

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