

Group Theoretical Methods Applied to Condensed Matter Problems

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Abstract

Group theoretical methods have important applications in many areas of condensed matter physics. As a first example, we present an investigation of “quadrupolar” phases in UPd_3 , a system which has a three-component order parameter resulting in an interesting phase diagram with an “octacritical” point. In our second example we discuss an unconventional (tetragonal) superconductor and show that the symmetry of its order parameter is revealed by spontaneous Josephson currents in a bicrystal ring experiment. The final example addresses polymer dynamics through an exact enumeration procedure for interactions and relative motion of two polymer segments on a lattice.

1 Quadrupolar phases in UPd_3

In the absence of external fields, UPd_3 , a hexagonal crystal with space group $G = P6_3/mmc$, undergoes a continuous phase transition at a temperature $T_1 \approx 7\text{K}$ (cf. Ref. [1] and references therein). According to Landau’s theory [2], continuous phase transitions are characterized by an order parameter η , which belongs to an irreducible representation of the group G . The order parameter is zero in the phase of higher symmetry (disordered phase) and changes continuously at the critical point to a non-zero value in the phase of lower symmetry (ordered phase). From an analysis of neutron scattering data, Walker *et al.* [1] determined the symmetry of the order

parameter and concluded that its three components describe the ordering of the electric quadrupole moments of the uranium ions and a simultaneous ion displacement along three equivalent directions in the basal (x, y) plane of the crystal.

The “Landau free energy” is a variational free energy expressed as a power series in the components η_i , which is invariant under the symmetry operations of the group G and respects thermodynamic stability requirements [2]. In the presence of symmetry-breaking fields, e.g. stress or magnetic fields, coupling terms (invariant under operations of G) between the order parameter and the applied fields are included, resulting in a Landau free energy [4]:

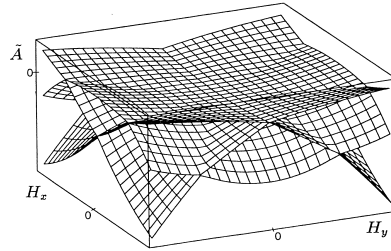
$$F = \tilde{A} \sum_{i=1}^3 \eta_i^2 + B \left(\sum_{i=1}^3 \eta_i^2 \right)^2 + C \sum_{i \neq j} \eta_i^2 \eta_j^2 + 2f\eta_1^2 + (-f + g)\eta_2^2 + (-f - g)\eta_3^2, \quad (1)$$

where $\tilde{A} = \alpha(T - T_1) + \beta$, T is the temperature, $\alpha > 0$ is a constant, and where the coefficients β , f , and g depend on the external fields. By minimizing the free energy, Eq. (1), and testing the solutions for thermodynamic stability, we arrive at the phase diagram for UPd₃ depicted in Fig. 1. The surfaces shown in Fig. 1 are surfaces of continuous phase transitions. At high temperatures, the system is completely disordered ($\eta_i = 0$, $i \in \{1, 2, 3\}$). As the temperature is lowered, the system will, in general, undergo three phase transitions in which the components η_i are “activated” one by one. A closer look at the phase diagram shows that, for $H_x = 0$ or $H_y = 0$, the critical surfaces meet in lines of “tetracritical” points, that is critical points at which four phases coexist. Only two transitions are expected under the circumstances and have indeed been found experimentally [1, 4]. The tetracritical lines meet at the point where $H_x = H_y = 0$, leading to the coexistence of eight distinct quadrupolar phases at a single critical point, an “octacritical” point.

Fluctuations of the order parameter in the vicinity of the critical points are not taken into account by the Landau theory of phase transitions, which is a mean-field theory. These fluctuations have the potential to change the phase diagram quantitatively and qualitatively. For our system [3], however, renormalization group calculations [5] show that the shape of the phase transition surfaces changes, but that the qualitative conclusions drawn here remain valid.

Figure 1:

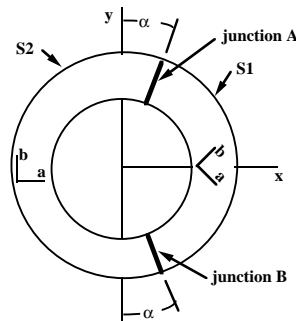
Phase-transition surfaces in the space of the temperature variable \tilde{A} and magnetic-field components H_x and H_y .



2 Josephson tunneling in high- T_c superconductors

The symmetry of the order parameter Ψ in unconventional (high temperature as well as heavy fermion) superconductors has raised a lot of interest (cf. [6]) since it poses restrictions on the possible (and as yet undetermined) microscopic mechanisms for unconventional superconductivity. Typical high-temperature superconducting materials have a layered structure, where most of the superconducting “condensate” is located in planes perpendicular to the c -axis of the crystal. Hence, the symmetry operations that leave the c -axis of the crystal invariant are of particular importance. For tetragonal high- T_c materials, i.e. materials with four-fold symmetry about the c -axis, the superconducting state is called (generalized) s -wave, if Ψ is invariant under rotations by $\pi/2$ about the c -axis and (generalized) d -wave if it changes sign under such rotations.

Figure 2: Experimental geometry to test for s -wave versus d -wave superconductivity in tetragonal systems [7]. S_1 and S_2 are tetragonal superconductors; a and b indicate their basal (x, y) plane unit cells; A and B are Josephson junctions; the angle α is chosen so that $\alpha \neq 0$, $\alpha \neq \pi/4$.



The Josephson current across a junction between two superconductors is a sensitive probe for the symmetry of the order parameter, but often additional assumptions have to be made to evaluate experimental results. To test for the symmetry of the order parameter based on symmetry arguments alone, we proposed [7] the experimental geometry depicted in Fig. 2. The superconductors S_1 and S_2 consist of the same tetragonal material, both with their c -axis perpendicular to the plane of the paper, but they are oriented so that the basal plane unit cell (spanned by \mathbf{a} and \mathbf{b}) of S_2 is rotated by an angle $\pi/4$ with respect to that of S_1 . The interfaces between S_1 and S_2 form the Josephson junctions A and B . Requirements of gauge invariance and time-reversal symmetry yield an expression for the variational free energy (to lowest order) associated with the interfaces:

$$F = c_A(\Psi_{1A}\Psi_{2A}^* + \Psi_{1A}^*\Psi_{2A}) + c_B(\Psi_{1B}\Psi_{2B}^* + \Psi_{1B}^*\Psi_{2B}), \quad (2)$$

where Ψ_{1A} is the order parameter of superconductor S_1 at Josephson junction A , etc., and where c_A and c_B are real. The experimental geometry in Fig. 2 is invariant under rotations (C_{2x}) by π about the horizontal x -axis, consequently the free energy F has to be invariant under C_{2x} . What happens to the order parameter under such rotations? If Ψ has s -wave symmetry, then it is invariant under C_{2x} implying $c_A = c_B$ in Eq. (2). If, however, Ψ has d -wave symmetry, then either Ψ_1 or Ψ_2 changes sign

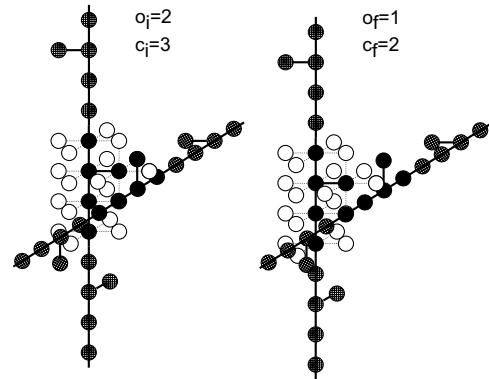
under C_{2x} implying $c_A = -c_B = e^{i\pi}c_B$. The phase difference of π between the two junctions generates a spontaneous current around the ring and a magnetic flux of half a magnetic flux quantum $\frac{1}{2}\Phi_0$ through the ring. Hence, if the symmetry of the order parameter is s -wave, no spontaneous magnetic flux will be generated in the ground state, while a spontaneous flux of $\frac{1}{2}\Phi_0$ is expected for the case of d -wave symmetry.

This experiment has since been carried out by Tsuei and coworkers [8] who fabricated a superconductor of appropriate geometry, carefully measured the magnetic flux over the sample, and showed unambiguously the d -wave symmetry of the order parameter for the tetragonal high-temperature superconductor $Tl_2Ba_2CuO_{6+\delta}$.

3 Exact enumerations of polymer segment configurations

In classical liquids, the contributions to thermodynamic properties arising from thermal motion can be separated from those due to interactions between the particles [2]. Lattice models, where each molecule occupies a fixed number of contiguous sites on a crystal lattice, voids allow for compressibility, and non-bonded nearest neighbor sites interact through energies ϵ_{ij} , are often employed to obtain tractable theories that still capture the essential features of interacting fluids. Such a lattice model is used here to study the effect of small-scale chain structure on the dynamic properties (e.g. the viscosity) of chain molecules (polymers) [9]. We place short chain segments of two molecules on a simple cubic lattice and exactly enumerate their interactions [10] and relative movements to estimate the “probability for segmental motion P ” which is inversely proportional to the viscosity, for example.

Figure 3: Combined configurations of two PEP chain segments before and after displacement of chain two (horizontal). The filled circles indicate carbon atoms with their attached hydrogens, the heavy lines represent chemical bonds, the open circles are the nearest neighbor (n.n.) sites of the repeat unit of interest of chain one (vertical). Chain two occupies $o_i = 2$ ($o_f = 1$) n.n. sites and makes $c_i = 3$ ($c_f = 2$) contacts with chain one before (after) displacement, see left (right) figure.



We employ representations of the cubic group O_h to generate all distinct conformations of single, straight chain segments of a fixed length and all distinct combined configurations of two such conformations. The use of group theoretical methods is essential in recognizing symmetry-related configurations to reduce the number of configurations treated explicitly in the simulation and to avoid double counting. A single

step in the enumeration procedure is illustrated in Fig. 3 for PEP, a saturated hydrocarbon (polyolefin) with a methyl group on every fourth carbon in the backbone. During the simulation, statistics are collected on the frequency of the initial state, characterized by occupation and contact numbers (o_i, c_i) , and the final states (o_f, c_f) that can be reached from (o_i, c_i) without overlap. These statistics are then evaluated taking energetics, temperature and density effects into account. A comparison with experimental data for a variety of polyolefins [9] shows that this approach gives a good qualitative representation of the effect of small scale architecture, temperature and pressure on the dynamic properties of polymers.

Acknowledgments

Financial support through a grant from the Natural Sciences and Engineering Council of Canada (UPd₃ and Josephson tunneling) and a Faculty Research Grant from the University of Akron (polymer dynamics) are gratefully acknowledged.

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