6. Phase Transitions in Chemisorbed Systems

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Microscopic theories are developed for condensed matter systems undergoing phase transitions. Phase diagrams and other macroscopic properties are deduced using renormalization-group techniques and other rigorous or approximate methods of statistical mechanics.

6.1 Phase Diagrams for Oxygen on Ni(100), SnTe, and Uranium Pnictides

Joint Services Electronics Program (Contract DAAG29-83-K-0003)

Robert G. Caflisch, A. Nihat Berker

We have completed[1] our renormalization-group theory of epitaxial adsorption onto a square substrate, with nearest-neighbor exclusion, second- and third-neighbor pair and trio interactions. Our global phase diagram study has led us to raise, for the first time, the possibility of two distinct 2x2 overlayer phases, characterized respectively by uniaxial and biaxial symmetry-breaking. The latter phase is novel, having four different sublattice coverages. Our phase diagrams exhibit 2x1, 2x2, and $\sqrt{2} \times \sqrt{2}$ ordered phases and a disordered phase. Thus, all three ordered structures observed with oxygen on nickel (100) are obtained within the same phase diagram in the coverage and temperature variables. One of these, the 2x1 phase, has a high entropy content, appears only at intermediate temperatures, and cannot be seen by classical theories. Other cross-sections of the global phase diagram, summing to six distinct topologies, may be applicable to chemisorbates such as oxygen, sulfur, selenium, or tellurium, on substrates such as nickel, copper, tungsten, or platinum (100). First- and second-order phase transition lines are punctuated by tricritical, critical-end, bicritical, and tetracritical points. Reentrant tricriticality, another new phenomenon, is found, yielding closed-loop coexistence regions.

To obtain the above results, we developed the renormalization-group treatment of competing atomic further-neighbor interactions. It now appears that our approach can yield the phase diagrams of a variety of other, bulk, condensed matter systems. Specifically, two such studies have been

initiated. First, the local structural degrees of freedom of the compound SnTe have been mapped onto an Ashkin–Teller model with thermal vacancies. This mapping already explains in simple energy–entropy terms the rhombohedral transition of this material. This project is pursued in collaboration with K. Rabe and J.D. Joannopoulos. *Ab initio* total energy calculations will be combined[2] with renormalization–group statistical mechanics. In another project, in collaboration with P. Erdös, the magnetic orderings of uranium pnictides are explored via our prefacing/renormalization–group mappings.

6.2 Metal–Insulator Transitions and the Spin–3/2 Ising Model

Joint Services Electronics Program (Contract DAAG29-83-K-0003)
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The metal–insulator transition has traditionally been described by the Hubbard Hamiltonian which includes a hopping term favoring the metal state and a Coulomb interaction. The solution of this model in d>1 dimension is quite difficult. We have initiated a study in which (1) the Hubbard Hamiltonian is mapped, approximately, onto a four–state classical model, and (2) the latter, which is a generalized spin–3/2 Ising model, is subjected to a position–space renormalization–group analysis. Our preliminary work indicates a phase diagram with metal, antiferromagnetic insulator, and paramagnetic insulator phases, in a critical end–point topology.

6.3 Phase Transitions in Potts Models with Broken Translational Invariance

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David Andelman, Daniel Blankschtein, Mehran Kardar, Miron Kaufman, A. Nihat Berker

We have established in our previous works that surface phase transitions can be modeled, in detail, by Potts models. During the last year, the critical amplitudes of the free energy of these models were studied[3,4] as a function of the number q of local states, in two dimensions and on the exactly solvable diamond hierarchical lattice.[5] Numerical renormalization–group and analytical duality–transformation techniques were employed. It was found that this amplitude diverges at an infinite number of values q_n, introducing logarithmic corrections to the critical singularities. In each interval (q_n, q_{n+1}), there is a value $\hat{q}_n$ where the amplitude vanishes, changing the quantitative nature of the singularity. Possible implications to the gelation and vulcanization of polymers were discussed. Other works on exactly solvable Hamiltonians have included the crossover to behavior imposed by long–range interactions, with interesting multicritical consequences,[6,12] and the construction of a sequence of hierarchical lattices which converge to ordinary Bravais lattices.[7]

We had also noted[8] that in adsorbed systems, substrate imperfections generate quenched random

fields, with strong effects on phase transition behavior. Thus, Potts models were studied[9] in the presence of random fields, which locally prefer alignment into any one of the q states. In d dimensions, the transition is expected to become first order for $q>q_c(d)$. As in the non-random case, mean-field theory gives $q_c(d) = 2$ for all d. Fluctuations are argued to shift the non-random value, $q_c^0(d)$, into a significantly higher value, $q_c(d)$. Accordingly, for $q_c^0(d)<q<q_c(d)$ quenched impurities are expected to turn the first-order transition into a second-order one. In three dimensions, this probably includes the experimentally realizable cases q = 3: diluted $SrTiO_3$ under a [111] uniaxial stress and q = 4: diluted NdSb, NdAs, CeAs, etc. under a [111] magnetic field.

We have also discovered[10] that the effective dimensional lowering caused by random fields can be simulated by another means of breaking translational invariance. In a rigorous statistical mechanical treatment,[10] the translational invariance of equivalent-neighbor Potts models was removed by introducing a Cayley-tree interaction K. For a range of K, the first-order transition persists, until a novel tricritical point, followed by continuously evolving second-order transitions. This is analogous to a continuous dimensional lowering.

6.4 Multicritical Phenomena in Cubic Symmetry Systems

Joint Services Electronics Program (Contract DAAG29-83-K-0003)
Robert G. Caflisch, Daniel Blankschtein

Phase transitions which are predicted to be first-order by the classical Landau theory can in fact be driven second-order by critical fluctuations. This fluctuation-induced criticality occurs in cubic systems which are almost tricritical. Application of symmetry-breaking perturbations suppresses fluctuations and may restore first-order behavior via new types of tricritical points. We are currently studying the effects of uniaxial quadratic symmetry-breaking perturbations on a three-component Hamiltonian with cubic symmetry present up to sixth order. We find that even at the mean-field level the competitions between the quadratic, fourth-order, and sixth-order anisotropies produce novel bicritical and tetracritical-like phase diagrams. Phases of the type [1,0,0], and [1,1,1], and [x,x,z] are encountered. Fluctuations are now analyzed with renormalization-group theory, and new multicritical phenomena are expected. The cubic phase diagrams are realizable experimentally by applying uniaxial stresses or magnetic fields to systems exhibiting structural or magnetic phase transitions, such as $KMnF_3$, $RbCaF_3$, $BaTiO_3$, MnO, TbP, etc.

6.5 Hydrogen-Bonding in Polymer Solutions: Reentrant Miscibility and Conformational Equilibria

Joint Services Electronics Program (Contract DAAG29-83-K-0003)
Raymond E. Goldstein

A theory is presented[11] which describes reentrant miscibility transitions[13] in solutions of polar polymers. These transitions are driven by orientationally specific interactions such as hydrogen bonds. The theory is within the context of the Flory-Higgins approach to solubility transitions. Pair interactions are controlled by a two-level equilibrium (bonded and non-bonded states) with appropriate energy and entropy terms. The results are in qualitative agreement with experiments on systems such as polyethylene oxide + water.

Correspondences are shown[11] between the microscopics of polymer conformational transitions (e.g., helix-coil transitions of polypeptides) and solubility phase transitions. Experiments are proposed to elucidate the roles of hydrogen bonding in molecular and polymer mixtures, to investigate new types of solubility transitions in polymer solutions, and to determine the interplay of conformational and solubility equilibria.

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7. Optics and Quantum Electronics

A. Nonlinear Phenomena

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7.1 Picosecond Optical Signal-Sampling Device

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The goal of the research is to develop prototype optical waveguide devices that operate at rates of many tens of Gigahertz. A 20 GHz Mach-Zehnder waveguide interferometric sampler operating at λ = 6328 Å in $LiNbO_3$ has been built and tested.[1,2] Since the power throughput of the device was too small to permit direct detection of the output samples by Second Harmonic Generation, the operation of the device was monitored by observing the optical spectrum of the output. The observed spectrum was consistent with the conclusion that the sampler produced 19 ps FWHM pulses with a 97 percent depth of modulation.

Construction of Mach-Zehnder waveguide interferometers can be achieved either by the use of waveguide Y's or by means of sections of straight coupled waveguides.[3] To construct compact devices, the Y-section must be made as short as possible. A typical length is of the order of a few millimeters. Shortening of the structure leads to increased radiation loss. The optimization of a design requires knowledge of the radiation loss produced in the waveguide Y's. We have carried out such a study with a new approach, the socalled "Volume Current Method".[4,5] Previous analyses of radiation loss in bent fibers cannot be used because they require matching of the radiation field solution to the nearfield surrounding the structure over a coordinate surface separating the two regions. Only few systems have the requisite degree of symmetry.

Since much of our device work uses the Mach-Zehnder waveguide interferometer, ways of constructing it and fine-tuning it after fabrication are of special interest. Kogelnik and Schmidt have

[1] Visiting Professor

shown that a coupled waveguide structure can be adjusted after fabrication via $\Delta\beta$ coupler principle. It is of interest to extend this principle to waveguide structures containing more than two waveguides, such as the waveguide Y constructed of three coupled waveguides.[3] We have shown that the principle is extendable and a $\Delta\beta$-type three-waveguide coupler is currently in the testing stage.

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7.2 Devices for High-Rate Optical Communications

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Clifton G. Fonstad, Hermann A. Haus

(c) The Waveguide Lens

Recently, a great deal of attention has been devoted to laser diode arrays that emit coherently, so that their entire output power can be focused into a diffraction limited spot.[1-3] One may ask the question whether it is possible to devise a passive, coupled waveguide system that would be capable of combining the power of the array into one "output" waveguide. Our theory of coupled waveguides is well adapted to provide the answer to such a question. We found that it is possible to combine all the power entering a N-th order planar coupled waveguide array (N is odd) into the center waveguide using axially uniform guides by proper choice of waveguide coupling and detuning in the following two cases.[4]

(a) The input excitations are all equal in magnitude and in phase.

(b) The input excitations are all equal in magnitude and alternate in phase by π.

The latter case is of most interest because diode arrays prefer this mode of operation. We plan to test the idea in a waveguide array fabricated in $LiNbO_3$.

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