

6. Phase Transitions in Chemisorbed Systems

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Surfaces and interfaces abound in our physical environment, and as systems which are low dimensional and therefore fluctuation dominated, embody fundamental problems of many-body physics. Our research group is studying a variety of low-dimensional and fluctuation-dominated systems. Such studies start with microscopic descriptions, such as the interactions of an overlayer in the presence of a constraining substrate, or the configuration energies and entropies of a helix-coil polymer immersed in an electrolyte. The eventual outcome is macroscopic, measured or measurable properties. Another important outcome is the understanding of mechanisms generic to many-body physics.

Through the discovery and development of the renormalization-group method, extraordinary advance has been achieved in recent years in phase transitions and critical phenomena. This approach successfully deals with a large number of coupled degrees of freedom in a stepwise manner, by thinning out a fraction of the degrees of freedom, and repeating this operation over and over. Thus, our program utilizes the renormalization-group method, but also any other theoretical tool as may be necessary. Important technical advances have been achieved in this respect.

6.1 Oxygen on Nickel and other Chemisorption Phase Diagrams

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Robert G. Caflisch, A. Nihat Berker

Epitaxial adsorption onto a square substrate is studied with a Hamiltonian including nearest-neighbor exclusion, second and third-neighbor pair and trio interactions. The resulting phase diagrams¹ exhibit 2×2 , $\sqrt{2} \times \sqrt{2}$, and 2×1 ordered phases and a disordered phase. Thus, all three ordered structures observed with oxygen on nickel (100) are obtained for the first time within the same phase diagram in the coverage and temperature variables. The 2×1 phase has an important entropy content and appears only at intermediate temperatures. Simple ground-state energy analysis

or classical mean-field calculations, therefore, completely miss this phase. Other cross-sections of our global phase diagram should 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 boundaries are evaluated, punctuated by tricritical, critical-end, bicritical, and tetracritical points. Reentrant tricriticality is found, yielding closed-loop coexistence regions. The possibility of two distinct 2×2 phases, with uniaxial order or a novel biaxial order, is raised for the first time. We use a Migdal-Kadanoff approximation on a cell system, with renormalization-group flows in sixteen energy levels.

In a separate work² in collaboration with Prof. J.D. Joannopoulos' group, total-energy ground state calculations are combined with renormalization-group analysis to predict the surface reconstruction of Si (100).

6.2 Commensurate-Incommensurate Phase Transitions, Domain Walls, and Helicity in Two-Dimensional Systems

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Mehran Kardar, A. Nihat Berker

Upon increased adsorption, registered overlayers become incommensurate with their substrate by forming high-density domain walls, which results in interactions (between domains) of a helical character. For this phenomenon, we introduced the helical Potts model, which successfully reproduced several experimental observations with krypton on graphite, from Prof. Birgeneau's group, and with krypton and deuterium coadsorbed on graphite. A q -state generalization of this model has been studied on the square lattice.³ At low temperatures, this model can be mapped onto the six-vertex model of Baxter in direct fields. This mapping indicates the presence of a modulated incommensurate phase. This phase exhibits a virtual ordering, in the sense that the correlations over large separations neither go to a non-zero constant, as in a truly ordered phase, nor do they decay exponentially to zero, as in a disordered phase. Instead, a weak algebraic decay of correlations occurs, with a critical exponent $\eta = 2/q^2$ at low temperature. A Lifshitz-like multicritical point is located where the registered, modulated, and disordered phases meet.

6.3 Multicritical Phenomena in Cubic Symmetry Systems

Joint Services Electronics Program (Contract DAAG29-80-C-0104)

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 tricritical points. We are currently studying the effect of off-diagonal, quadratic symmetry-breaking perturbations on cubic systems undergoing fluctuation-induced transitions. We expect a wide variety of bicritical and tetracritical-like phase diagrams, also featuring tricritical, critical and critical-end points. Our approach combines mean-field theory, large-anisotropy expansion, and renormalization-group analysis. The relevance of cubic models to oxygen chemisorbed on nickel (111) has been noted by other workers. The cubic phase diagrams may also be 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.

6.4 Crossover to Equivalent-Neighbor Multicritical Behavior

Joint Services Electronics Program (Contract DAAG29-80-C-0104)

Mehran Kardar, A. Nihat Berker

Exact solutions of models of many-body systems, though difficult to achieve, are of crucial importance to our understanding of physical phase transition phenomena. Our recently introduced central-limit minimization method, based on a new statistical mechanical proof, yields new classes of exactly solvable Hamiltonians. Using this method, systems with both short- and long-range interactions are solved exactly.⁴ Such situations could occur, for example, in chemisorption or surface reconstruction systems with short-range covalent bond formation and long-range dipolar couplings. Crossover from fluctuation-dominated to mean-field criticality is described in arbitrary spatial dimension. Phase diagrams are derived, with lines of classical and non-classical second-order transitions and first-order transitions, meeting at multicritical points and exhibiting new types of critical behavior.

6.5 Hydrogen-Bonding and Helix-Coil Transformations

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Raymond E. Goldstein, A. Nihat Berker

The conformational changes undergone by certain biological macromolecules, such as poly- γ -benzyl-L-glutamate in ethylene dichloride + dichloroacetic acid, are proposed to arise from the same interplay of energy versus entropy that causes lower critical-solution points in liquid mixtures, which have been studied extensively in this group. In these mixtures, hydrogen bonds between unlike molecules are responsible for the reappearance of a miscible (substitutionally long-range disordered) phase below a lower critical temperature, but concurrently with increased short-range orientational order, so that entropy is decreased according to the third law. This results

in closed-loop coexistence regions. Note that we have also predicted closed-loop coexistence regions in chemisorbed systems. In certain macromolecular solutions, an ordered helical state evolves into a random-coil state with decreasing temperature. This reversal from the expected ordering trend is explained by associating to the polymer-solvent hydrogen bonds, the role played by unlike-molecule bonds in liquid mixtures. A Potts model is used to carry out the statistical mechanics of these macromolecular solutions. Experiments to clarify the relationship outlined above are proposed.

6.6 Improved Renormalization-Group Transformations

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David Andelman, Raymond E. Goldstein, James S. Walker, A. Nihat Berker

In its rapid evolution to an everyday calculational tool, the renormalization-group method incorporates correlated fluctuations, but yet has become more amenable than classical approaches to many problems. This is certainly the case, for example, for the calculation of the multicritical, multistructure phase diagrams of chemisorbed systems described above. One approach which we have introduced is to map, by a so-called prefacing transformation, a system with complicated further-neighbor interactions onto one with complicated local degrees of freedom coupled by nearest-neighbor interactions, and readily renormalizable. This renormalization is most easily done by a Migdal-Kadanoff procedure. We have also investigated replacing the ad hoc bond-moving prescription of this approximation by a systematic procedure. The free energy is required to be preserved by matching perturbative series expansions. The approach is characterized by a small parameter, and can be order-by-order extended. A significant improvement is obtained over the standard Migdal-Kadanoff calculation, with little increased effort. A detailed application to q-state Potts models in two and three dimensions has been presented.^{5,6} In a most recent development, the bond-moving procedure is fixed by an exact finite-lattice calculation. The resulting renormalization-group transformation is applied to infinite, thermodynamic systems. This new method is most promising in that it produces quantitative results for three-dimensional systems.

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