1. Introduction

The frustrated spin-gas model with dipolar, van der Waals, and benzene-ring steric interactions is studied by Monte Carlo. Reentrant phase diagrams are obtained, with the sequence nematic-smectic A$_1$-nematic-smectic A$_2$-smectic C. The reentrance mechanism is in terms of interpenetrating order and disorder. Layer tilting is found to be due to permeation-rotation lock-in. The smectic A$_1$ and C phases occur in two versions, one pointing to in-plane domain formation. The phase diagrams are obtained by adapting the Lindemann melting criterion. Layer thicknesses, tilts, specific heats, and dimer concentrations are evaluated. The model explains three types of smectic C phases distinguished by tilt saturation. Results qualitatively agree with experiments.

2. Reentrance Phenomena

The occurrence of a less ordered phase at temperatures below those of a more ordered phase is, at first glance, surprising. Elementary thermodynamics has imprinted in us that the free energy, $F=U-TS$, is minimized at low temperatures $T$ by minimizing the internal energy $U$, which is usually accomplished by the system forming an ordered array, and at high temperatures by maximizing the entropy $S$, which is accomplished by the system sampling all of its possible states, abandoning the subspace of order. We should hasten to reassure that elementary thermodynamics still works: the paradox mentioned in the first sentence above is only an apparent one, and is conceptually dissolved by identifying long-range order and short-range order, which replace each other in these systems.

Liquid crystals are the physical systems in which this phenomenon of reentrance (the disordered phase of high temperatures "reenters" at temperatures below the intermediate temperatures of the ordered phase) has received much attention, after the experimental discovery by Cladis. Reentrance also occurs in very diverse other systems such as liquid mixtures,
spin-glasses, surface adsorbates, and magnets with crystal fields. It has turned out that the theoretical challenge posed by reentrant phase transitions is the converse of the challenge of critical exponent universality of two decades ago: Whereas universality of critical exponents in very diverse systems was eventually understood by the single mechanism of irrelevant thermodynamic fields in renormalization-group flows toward a fixed point, reentrant phase transitions have required a detailed microscopic understanding and model solving for each diverse system:

1. In liquid mixtures, the orientational correlations of the lower temperatures change the effective net interspecies interactions from repulsive to attractive, via hydrogen-bonding in mutually oriented interspecies pairs, thereby causing the phase separation of intermediate temperatures to reverse itself.

2. In spin-glasses, the saturation of short-range ferromagnetic order destroys long-range antiferromagnetic correlations and, simultaneously and conversely, the saturation of short-range antiferromagnetic order destroys long-range ferromagnetic correlations.

3. In krypton adsorbed on a graphite substrate, cooling is necessary for enough adsorption from the vapor to establish connectivity and (commensurate) order on the surface; but further cooling and, thereby, further adsorption introduces heavy and superheavy domain walls that disrupt and eventually destroy this order; even further cooling and adsorption creates a network of superheavy domain walls, which is incommensurate order.

4. In magnets with a quenching crystal field, ferromagnetic order can disappear at low temperatures due to the removal of local moments by the crystal field.

In liquid crystals, the closepacking inherent to the liquid inescapably leads to frustration with molecules that have dipole moments: in many local positional configurations of the molecules, different local orientational configurations equally minimize the energy. Another microscopic characteristic is molecular corrugation, amounting to a mutual substrate effect in nearest-neighbor molecules. The frustrated spin-gas model is a microscopic model that begins with incorporating these two characteristics, dipolar frustration and molecular corrugation. An approximate solution of the model has yielded reentrant phase diagrams, in qualitative agreement with experiments, up to the quadruply reentrant case of nematic-smectic A→nematic-smectic A I→smectic C as temperature is lowered. Calculated relative specific heats and layer thicknesses, and molecular dimer concentrations have also been in qualitative agreement with experiments.

We have considerably further developed the frustrated spin-gas model:

1. The solution of the model has been made less ad hoc, at the price of increased computation, by the use of Monte Carlo sampling. The phase diagrams are calculated by adapting to the nematic-smectic transition the Lindemann criterion of melting. Reentrant phase diagrams are obtained, and the microscopic mechanism for the intermediate-temperature existence of the smectic A I phase has become apparent, in terms of the interpenetrating coexistence of order and disorder. Specific heats, layer thicknesses, and molecular dimer concentrations are evaluated.

2. The model itself has been further developed by incorporating the aspect ratio of the benzene rings in the molecular cores and the resultant steric effects, in addition to the dipolar frustration. Thus, the smectic C phase, in the sequence nematic-smectic A→nematic-(smectic A I→smectic C as temperature is lowered, has been obtained and the microscopic mechanism for smectic C layer tilting has been found. It is the lock-in of permeational and rotational degrees of freedom, which are respectively influenced by dipolar interactions and benzene-ring steric hindrances. Layer tilt angles are evaluated. The microscopic model explains the long-standing catalogued experimental data of three types of smectic C phases distinguished by tilt saturation behavior.