Phase Transitions and Quantum Effects in Adsorbed Monolayers

P. Nielaba

Phase transitions in absorbed (two-dimensional) fluids and in absorbed layers of linear molecules are studied with a combination of path integral Monte Carlo (PIMC), Gibbs ensemble Monte Carlo (GEMC), and finite size scaling techniques. For a classical (nonadditive) hard-disk fluid the "critical" nonadditivities, where the entropy-driven phase separations set in, are presented. For a fluid with internal quantum states the gas–liquid coexistence region, tricritical, and triple points can be determined, and a comparison with density functional (DFT) results shows good agreement for the freezing densities. Linear $N_2$ molecules adsorbed on graphite (in the $\sqrt{3} \times \sqrt{3}$ structure) show a transition from a high-temperature phase to a low-temperature phase with herringbone ordering of the orientational degrees of freedom. The order of the transition is determined in the anisotropic planar–rotor model as a weak first-order transition. The effect of quantum fluctuations on the herringbone transition is quantified by PIMC and classical simulational methods. The values of the order parameter at low temperatures and the transition temperature are both lowered by roughly 10% due to quantum effects. Rounding effects of the phase transition in adsorbed layers of $(N_2)_x (CO)_{1-x}$ for $x < 7\%$ are analyzed by Monte Carlo (MC) methods, and the ground state ordering for the transition in the adsorbed pure CO system is discussed, from ab initio potentials.

KEY WORDS: adsorbed layers; Gibbs ensemble Monte Carlo; path integral Monte Carlo; phase transitions.

1. INTRODUCTION

Two-dimensional (2D) layers at surfaces have become an interesting field of research during the last decade [1]. Most of the phase transitions in these systems occur at fairly low temperatures, and for many aspects of the behavior quantum effects need to be considered. This holds in particular if one is concerned with adsorbed molecules at surfaces, since the molecules

---

2 Institut für Physik, Universität Mainz, D-55099 Mainz, Germany.
have internal degrees of freedom which need to be treated quantum-
mechanically even if the translational degrees of freedom can still be treated
classically. Linear N\textsubscript{2} molecules adsorbed on graphite (in the $\sqrt{3} \times \sqrt{3}$
structure) show a transition from a high-temperature phase to a low-
temperature phase with herringbone ordering of the orientational degrees of
freedom. In Section 2, the order of the transition is determined in the
anisotropic planar–rotor model by analysis of the correlation length $\zeta$
near the transition temperature $T_0$. The simulation data, extrapolated to $T_0$,
yield a large but finite $\zeta$ at $T_0$, demonstrating that the herringbone
ordering is a weak first-order transition. The effect of quantum fluctuations
on the herringbone transition is quantified by PIMC and classical simul-
tational methods. Quasiclassical and quasiharmonic calculations agree for
high and low temperatures, respectively, but only PIMC gives good results
over the entire temperature range. In Section 3, a study of the properties of
2D model fluids with GEMC techniques is presented. In particular, the
entropy-driven phase separation in the case of a nonadditive symmetric
hard-disk fluid is analyzed, and the critical line of nonadditivities as a func-
tion of the system density separating the mixing/demixing regions can be
located by a combination of GEMC with finite-size scaling techniques. A
comparison with a simple approximation is shown. PIMC and GEMC
techniques are then combined in order to locate the gas–liquid coexistence
densities for a fluid with classical degrees of freedom and internal quantum
states, a comparison with NVT-ensemble results and mean field (MF)
predictions is presented, and a DFT approach is outlined. In Section 4, the
random field-induced rounding of the Ising-type transition in physisorbed
(CO)$_{1-x}$(N\textsubscript{2})$_x$ mixtures is studied. Good qualitative agreement with
recent experiments is obtained with a simple model.

2. ORIENTATIONAL PHASE TRANSITIONS IN ADSORBED
MONOLAYERS

For many years adsorbed layers of N\textsubscript{2} on graphite have served as a
prototype example to study phase transitions in 2D. The phase diagram
[2] includes below 50 K a registered phase having a commensurate
($\sqrt{3} \times \sqrt{3}$) $R30^\circ$ structure. The orientations of the molecular axes undergo
in this phase an orientational phase transition at around 27 K to the “2-in”
herringbone phase, which retains the translationally ordered $\sqrt{3}$ structure
of the molecular centers of mass. The herringbone phase transition has
been investigated [3] by MC simulations using the anisotropic planar–
rotor (APR) model. The APR Hamiltonian [5]

$$H = K(N_2) \sum_{\langle i, j \rangle} \cos[2\varphi(R_i) + 2\varphi(R_j) - 4\Theta_{ij}]$$

(1)