

Statistical Thermodynamics, Molecular Modeling and Simulation: extended syllabus

Basic principles of statistical mechanics, ergodic hypothesis. Phase space.

Mathematical preface: Gaussian integral. Stirling formula (derivation). The saddle point method. Mathematical statistics – basic distributions: binomial, Poisson, normal. Mean value and fluctuation.

Microcanonical ensemble. Entropy as a measure of chaos. The relationship between statistical mechanics and thermodynamics. Conditions of equilibrium. Entropy of mixing. Gibbs paradox. Condition of validity of the (classical) Boltzmann statistics.

Canonical ensemble. Boltzmann's factor. Entropy. Classical partition function in the phase space. Application to ideal gas.

Ideal gas with internal degrees of freedom (non-interacting molecules). Vibration and rotation modes. Energy and heat capacity of individual contributions; low temperature and high temperature limit. Calculation of the equilibrium constant of chemical reactions in the ideal gas phase.

Virial and equipartition theorem. Grand canonical ensemble.

Discrete and continuous interaction models. Forces between molecules, force field (bonded and non-bonded forces, parameter setting, combining rules).

Nonideal behavior of substances. Correlation (distribution) functions. Structure factor. Virial expansion. The OZ integral equation.

Molecular dynamics: types of algorithms for different systems, integrators for continuous models (Verlet algorithm and equivalent formulas, time reversibility and energy conservation, integration error, Gear algorithms – briefly). Temperature in the microcanonical MD ensemble, constant temperature simulation (canonical and non-canonical methods and their properties and problems).

Monte Carlo method: MC integration and importance sampling. Metropolis algorithm (Markov chain, detailed balance and microreversibility), acceptance ratio. Random number generator.

Computer experiment (start, equilibration, error estimation). Periodic boundary conditions, nearest neighbors, long and short-range forces (corrections, Ewald summation, reaction field method), algorithms, optimization.

Advanced Monte Carlo methods: non-Boltzmann and preferential sampling, implementation of MC in various ensemble (microcanonical, isobaric, grandcanonical, Gibbs). Vibrating and rigid bonds, SHAKE algorithm.

Kinetic quantities in MD, equilibrium and non-equilibrium methods. Time autocorrelation function, Green–Kubo Formulas, Einstein's formulas using diffusivity as an example.