Some formulas and concepts of statistical physics

(Computational Chemistry and Materials Modeling, Skoltech 2014)

Ergodicity: $\lim_{T\to\infty} \int_0^T A(t)\,\mathrm{d}t$ does not depend on starting point.

Ensemble average: $\langle A\rangle = \int A(p,q)\rho(p,q)\,\mathrm{d}\Gamma$, where $\mathrm{d}\Gamma = \frac{\mathrm{d}p\,\mathrm{d}q}{(2\pi\hbar)^N}$.

Thermodynamic ensembles and energies: NVE (microcanonical, energy E or entropy S), NVT (canonical, free energy F), NPT (Gibbs free energy G), NPE (enthalpy H).

Fundamental thermodynamic relation: $T\,\mathrm{d}S \geqslant \delta Q = \mathrm{d}E + p\,\mathrm{d}V + \sum a\,\mathrm{d}A - \mu\,\mathrm{d}N$.

Heat capacity: $C = \frac{\delta Q}{\delta T} = T\frac{\mathrm{d}S}{\mathrm{d}T}$.

Canonical ensemble: $\rho(p,q) = \exp\left(\frac{F-H(p,q)}{kT}\right)$, $F = kT\ln Z$, $Z = \int \mathrm{e}^{-H(p,q)/kT}\,\mathrm{d}\Gamma$.

Quantum oscillator: $E_n = \hbar\omega\left(n+\frac{1}{2}\right)$, $Z = \left(2\sinh\frac{\hbar\omega}{2kT}\right)^{-1}$, $E = \frac{\hbar\omega}{2}\coth\frac{\hbar\omega}{2kT}$, $C/k = \left(\frac{\hbar\omega}{2kT}\,/\sinh\frac{\hbar\omega}{2kT}\right)^2$.