CHM 421/621 Statistical Mechanics

Lecture 20 Microcanonical Ensemble Examples

Formalisms of Statistical Mechanics

Lecture Plan

Basic Postulates

Counting microstates in an ideal gas

Boltzmann equation for entropy

Microcanonical Ensemble

Canonical Ensemble

Formalisms of Statistical Mechanics

Boltzmann equation for entropy

For a monatomic ideal gas

$$s = \frac{S}{N} = k_B \ln V + \frac{3}{2} k_B \ln U + C$$

$$\frac{P}{T} = ?$$

$$\frac{1}{T} = ?$$

$$C_V = ?$$

Formalisms of Statistical Mechanics

Boltzmann equation for entropy

System of N 2-level atoms

Each atom can be in one of two levels with energy 0 and ϵ

$$U = m\epsilon$$

$$\implies m = U/\epsilon$$

$$\Omega(U,V,N) =^N C_m = \frac{N!}{(N-m)!m!}$$

$$S = k_B \ln \Omega(U,V,N) = ?$$

$$\frac{1}{T} = ?$$

$$C_V = ?$$

Formalisms of Statistical Mechanics

Boltzmann equation for entropy

System of N 2-level atoms

$$\Omega(U,V,N) = ^N C_m = \frac{N!}{(N-m)!m!}$$

Employing the Stirling formula

$$\begin{aligned} S &= k_B \ln \Omega(U,V,N) \\ &= k_B \{\ln N! - \ln(N-m)! - \ln m!\} \\ &\approx k_B \{N \ln N - N - (N-m)\ln(N-m) + (N-m) - m \ln m + m\} \quad \text{For large } N \\ &= -k_B \left\{(N-m)\ln\left(\frac{N-m}{N}\right) + m \ln\left(\frac{m}{N}\right)\right\} \\ &= -Nk_B \{(1-\eta)\ln(1-\eta) + \eta \ln(\eta)\} \end{aligned}$$

where $\eta = \frac{m}{N} = \frac{U}{N\epsilon}$ fraction of excited atoms

Formalisms of Statistical Mechanics

Boltzmann equation for entropy

System of N 2-level atoms

$$S = -Nk_B\left\{(1-\eta)\ln(1-\eta) + \eta\ln\eta\right\}$$

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N}$$
$$= \frac{1}{N\epsilon}\left(\frac{\partial S}{\partial \eta}\right)_{V,N}$$
$$= \frac{k_B}{\epsilon}\ln\left(\frac{N\epsilon}{U} - 1\right)$$

Or

$$U = \frac{N\epsilon}{e^{\beta\epsilon}+1}$$

$$\beta = \frac{1}{k_B T}$$

Note that $1 < \dfrac{N\epsilon}{U} < \infty$

For $1 < \dfrac{N\epsilon}{U} < 2 \qquad 1/T < 0$

=> temperature is negative!!

Population inversion regime.
Can occur in isolated nuclear spin systems

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{V,N}$$
$$= Nk_B\beta^2\epsilon^2\frac{e^{\beta\epsilon}}{(1+e^{\beta\epsilon})^2}$$