Classical Ensembles

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In material research, the subject is a collection of vast number of individual “particles” that follow either the classical mechanic rules of motion or quantum mechanic rules of motion depending on the specific macro-state function that the research is called for. This article focuses on those material properties that are determined by the classical micro-state movements.

Fundamental Properties

Energy. The energy of a particle is comprised of kinetic energy and potential energy. The sum of the energy is E_i. The energy of the ensemble is the sum of energies of all N particles:

$$E = \sum_{i=1}^{N} E_i$$

The total number of particles is enormous (10^{23}).

Entropy: Entropy of the ensemble is the logarithmic total number of the micro states (Ω) at a given energy. The number of micro state is a function of energy (E) and volume (V), of the ensemble.

$$S = k_B \log(\Omega)$$

where k_B is the Boltzmann constant so that entropy has a meaningful unit from the logarithmic number. Josiah Willard Gibbs further gave the following expression of entropy using the probability distribution (p_i) of the micro states.

$$S = -k_B \sum_{i=1}^{\Omega} p_i \log(p_i)$$

Temperature: Temperature is increase in energy by an increase in unit entropy.

$$T = \frac{\partial E}{\partial S}$$

Pressure: Pressure is increase in energy by an increase in unit volume.

$$p = \frac{\partial E}{\partial V} = \frac{\partial E}{\partial S}\frac{\partial S}{\partial V} = T\frac{\partial S}{\partial V}$$

Since Ω is a function of energy and volume, entropy is also a function of energy and volume of the ensemble. For the ensemble undergoing a small change, the change in entropy is:

$$dS = \frac{\partial S}{\partial E}dE + \frac{\partial S}{\partial V}dV$$

Substituting definitions of T and p, one has another expression of *the first law of thermodynamics*:

$$dE = TdS - pdV$$

Helmholtz Free Energy: This energy is not free with no cost, but “available energy” to do work.

$$F = E - TS$$

$$dF = dE – d(TS) = TdS - pdV - SdT - TdS = -SdT - pdV$$

$$p = -\left.\frac{\partial F}{\partial V}\right|_T$$

Boltzmann Distribution

The micro state distribution function (p_i) can be solved using the variational principle by maximizing the entropy of the ensemble subjecting to the constraints that the total energy is the same and the sum of the probabilities is one.

$$p_i = \max_{p_i}\left(-k_B \sum_{i=1}^{\Omega} p_i log(p_i)\right)$$

$$1 = \sum_{i=1}^{\Omega} p_i$$

$$E = \sum_{i=1}^{\Omega} p_i E_i$$

Using α as the Lagrange multiplier for the first constraint and β for the second, and change the maximizing to minimizing the negation of entropy, p_i is solved by setting the derivative be zero:

$$p_i = e^{k_B + \alpha} e^{-\beta E_i}$$

Define Z as the *partition function* of the Boltzmann distribution:

$$\frac{1}{Z} = e^{k_B + \alpha}$$

$$Z = \sum_{i=1}^{\Omega} e^{-\beta E_i}$$

Bridging Macro State and Micro State

Energy

$$E = \sum_{i=1}^{\Omega} p_i E_i = \frac{1}{Z}\sum_{i=1}^{\Omega} e^{-\beta E_i} E_i = \frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\frac{\partial log(Z)}{\partial \beta}$$

Entropy

$$S = -k_B \sum_{i=1}^{\Omega} p_i \log(p_i) = \frac{k_B}{Z} \sum_{i=1}^{\Omega} e^{-\beta E_i} \left[\beta E_i + log(Z)\right] = k_B \beta E + k_B log(Z)$$

Temperature

$$\frac{1}{T} = \frac{\partial S}{\partial E} = k_B \beta$$

Helmholtz Free Energy.

$$F = E - TS = E - T\left(k_B \beta E + k_B log Z\right) = -k_B T log Z$$

Pressure

$$p = -\left.\frac{\partial F}{\partial V}\right|_T = k_B T \frac{\partial log Z}{\partial V}$$

Ideal Gas

The ideal gas molecules are far apart and there is no potential energy between the molecules. Therefore the energy of the gas molecule is $E(p)$, where p is the momentum. Also, N is very, very large, the summation in the partition function may be replaced by an integration as if the function is continuous:

$$Z = \int_{x,p} d^3x d^3p \, e^{-\beta E(p)} = V^N \int_p d^3p \, e^{-\beta E(p)} = V^N KE$$

$$log Z = N log V + log\left(KE\right)$$

$$p = k_B T \frac{\partial log Z}{\partial V} = k_B T \frac{N}{V} = \rho k_B T$$

$$pV = N k_B T$$

where KE is the kinetic energy integral that vanishes after differentiation since it does not depend on the coordinates of gas molecules. In fact,

$$KE = \int_p e^{-\beta p^2/(2m)} d^3p = \left(\sqrt{\frac{2m\pi}{\beta}}\right)^{3N}$$

$$E = -\frac{\partial log(Z)}{\partial \beta} = \frac{3}{2}\frac{N}{\beta} = \frac{3}{2} N k_B T$$

This is called equipartition of energy. Therefore, the average energy of each degree of freedom in a system at temperature T is $k_B T/2$.

Classical Harmonic Oscilator

The oscillator has both kinetic energy and potential energy:

$$E_i = \frac{p^2}{2m} + \frac{kx^2}{2}$$

where m is the mass of the oscillator and k the spring constant.

$$Z = \int_{x,p} dxdp\, e^{-\beta p^2/2m}\, e^{-\beta kx^2/2} = \int_p dp\, e^{-\beta p^2/2m} \int_x dx\, e^{-\beta kx^2/2}$$

Each of the integrals can be expressed in the Gaussian form by variable substitution:

$$\int dxe^{-ax^2} = \sqrt{\frac{\pi}{a}}$$

$$Z = \sqrt{\frac{2m\pi}{\beta}}\sqrt{\frac{2\pi}{k\beta}} = \frac{2\pi}{\omega\beta}$$

where ω is the natural frequency of the oscillator.

$$E = -\frac{\partial logZ}{\partial\beta} = \frac{1}{\beta} = k_B T$$

Diatomic Gas

The partition function is a product of translation, rotation and vibration:

$$Z = Z_{tran} Z_{rot} Z_{vib}$$

where the energy of rotation with a moment of inertia, I, is:

$$E_{rot} = \frac{p_\theta^2}{2I} + \frac{p_\phi^2}{2I\sin^2\theta}$$

$$Z_{rot} = \int d\theta\, d\phi\, dp_\theta\, dp_\phi\, e^{-\beta E_{rot}} = \sqrt{\frac{2\pi I}{\beta}} \int_0^\pi d\theta \sqrt{\frac{2\pi I\sin^2\theta}{\beta}} \int_0^{2\pi} d\phi = \frac{8\pi^2 I}{\beta}$$

$$E_{rot} = -\frac{\partial logZ_{rot}}{\partial\beta} = \frac{1}{\beta} = k_B T$$

$$E = E_{tran} + E_{rot} + E_{vib} = \frac{3}{2}k_B T + k_B T + k_B T = \frac{7}{2}k_B T$$

Summary of Classical Ensembles

The partition functions of classical ensembles are derived by maximizing the total entropy subjecting to constraints of 1) unity of sum of probabilities, 2) energy conservation (canonical ensemble), and 3) mass conservation (grand canonical ensemble). The composition of the energy term also affects the partition function. The table below provides a brief summary, where λ is the *thermal de Broglie wavelength*:

$$\lambda = \sqrt{\frac{2\pi\hbar^2}{mk_BT}}$$

ensemble	**energy**	**log partition function**
Ideal gas	$\sum^{3N}\frac{p^2}{2m}$	$N\log\left(\frac{V}{\lambda^3}\right)$
mass conservation	$\sum^{3N}\frac{p^2}{2m}-\mu N$	$N\log\left(\frac{Ve^{\beta\mu}}{\lambda^3}\right)$
diatomic gas	$\sum^{3N}\frac{p^2}{2m}+\frac{m\omega^2x^2}{2}+\frac{p_\theta^2+p_\phi^2/\sin^2\theta}{2I}$	$N\log\left[\left(\frac{V}{\lambda^3}\right)\left(\frac{k_BT}{\hbar\omega}\right)\left(\frac{2Ik_BT}{\hbar^2}\right)\right]$
interacting gas	$\sum^{3N}\frac{p^2}{2m}+U(x_m-x_n)$	$N\log\left(\frac{V}{\lambda^3}\right)+\frac{N\rho U_0}{2k_BT}$
potential field	$\sum^{3N}\frac{p^2}{2m}+U(x)$	$N\log\left(\frac{V}{\lambda^3}\int d^3xe^{-\beta U(x)}\right)$