Problem III.6 | Sheet 1

(a) Microcanonical ensemble.

The ensemble describes an isolated system with a fixed number of particles and a fixed total energy E.

The numbers of particles n_+ and n_- with energies ε and $-\varepsilon$, respectively, are clearly constricted by the two relations:

- $E = n_+ \varepsilon - n_- \varepsilon$
- $N = n_+ + n_-$

Defining the quantity: $x = \frac{E}{N\varepsilon}$ ($\propto$ energy per particle)

we find: $n_+ = \frac{N(1+x)}{2}$

$$n_- = \frac{N(1-x)}{2}$$

The partition sum is just THE number of microstates consistent with these constraints, and is equal to the number of ways of choosing, say, n_+ particles from N:

$$Z_\mu(E,N) = \binom{N}{n_+} = \frac{N!}{n_+!\,n_-!}$$

$$S_\mu(E,N) = \ln Z_\mu$$

In the limit of large N: $\ln N! \approx N\ln N - N$,

the entropy per particle

$$s_\mu = \lim_{N\to\infty}\left(\frac{S_\mu}{N}\right) = \ln 2 - \frac{1}{2}(1+x)\ln(1+x) - \frac{1}{2}(1-x)\ln(1-x)$$

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(b) <u>Canonical ensemble</u>. describes a system with a fixed number of particles in contact with a heat bath at a fixed temperature.

$$Z(T,N) = \sum_{n_+=0}^{N} \binom{N}{n_+} e^{-\beta\varepsilon n_+} e^{\beta\varepsilon(N-n_+)} =$$
$$= \left(e^{-\beta\varepsilon} + e^{\beta\varepsilon}\right)^N$$

$F = -T \ln Z = E - TS$, and E is defined as the mean value

$$E \equiv \langle E \rangle = -\left(\frac{\partial(\ln Z)}{\partial \beta}\right)_N = -N\varepsilon \tanh(\beta\varepsilon)$$

The mean energy per particle:

$$E_p = \frac{\langle E \rangle}{N}, \text{ with } x = \frac{E}{N\varepsilon} = -\tanh(\beta\varepsilon).$$

To obtain the entropy, we first need to solve the relation for x to find the temperature in terms of x:

$$\beta\varepsilon = \frac{1}{2}\ln\left(\frac{1-x}{1+x}\right) = \frac{1}{2}\left[\ln(1-x) - \ln(1+x)\right]$$

Thus:

$$E = xN\varepsilon$$
$$F = -T\ln Z = -NT\left[\ln 2 - \frac{1}{2}\ln(1+x) - \frac{1}{2}\ln(1-x)\right]$$
$$S = \frac{E-F}{T} = N\left[\ln 2 - \frac{1}{2}(1+x)\ln(1+x) - \frac{1}{2}(1-x)\ln(1-x)\right]$$
$$s = \frac{S}{N} \text{ same as (a)}$$

Problem III.6 | Sheet 3

(c) GCA: describes a system in equilibrium with a reservoir, with which it can exchange both energy and particles.

Denote: $z = e^{\beta\mu}$, a.k.a. FUGACITY

$$\Xi(T,\mu) = \sum_{N=0}^{\infty} z^N Z(T,N) = \frac{1}{1 - z(e^{\beta\varepsilon} + e^{-\beta\varepsilon})}$$

$\Omega = T \ln \Xi$, $\Omega = TS - E + \mu N$, where

$$N = \langle N \rangle = z \left(\frac{\partial (\ln \Xi)}{\partial z} \right)_\beta = \frac{z(e^{\beta\varepsilon} + e^{-\beta\varepsilon})}{1 - z(e^{\beta\varepsilon} + e^{-\beta\varepsilon})}$$

$$E = \langle E \rangle = -\left(\frac{\partial (\ln \Xi)}{\partial \beta} \right)_z = -N\varepsilon \tanh(\beta\varepsilon)$$

Set $x = \frac{E}{N\varepsilon} = -\tanh(\beta\varepsilon)$.

First, obtain
$$\beta\varepsilon = \frac{1}{2}\left[\ln(1-x) - \ln(1+x)\right]$$
$$\beta\mu = \ln\left(\frac{N}{N+1}\right) - \ln 2 + \frac{1}{2}\left[\ln(1+x) + \ln(1-x)\right]$$

we have:

$$E = N\varepsilon x$$
$$\Omega = T \ln \Xi = T \ln(N+1)$$
$$S = \frac{1}{T}(\Omega + E - \mu N) =$$
$$= N\left[\frac{\ln(N+1)}{N} + \ln\left(1 + \frac{1}{N}\right) + \ln 2 - \frac{1}{2}(1+x)\ln(1+x) - \right.$$
$$\left. - \frac{1}{2}(1-x)\ln(1-x)\right]$$

$s = \lim_{N\to\infty} \left(\frac{S}{N}\right)$ is apparently the same as before.

In THERMODYNAMIC LIMIT, the th. functions given by all three ensembles are identical, provided that one deals with intensive quantities (i.e. entropy per particle).