

Conjunto gran canónico

When a system is open to the surrounding environment, both the energy and particle number of the system can fluctuate. In that case, the system will be in equilibrium with the environment if the temperature and chemical potential (of each kind of particle) are the same in the system and the environment. The probability distribution and the thermodynamic properties of particles in open systems are given by the grand canonical ensemble,

Consideramos ahora un sistema S en contacto con un reservoir R, pero ahora los sistemas S y R pueden intercambiar partículas y energía. El reservoir está caracterizado por una temperatura T y un potencial químico μ . El sistema global $G = R+S$ está aislado.

Sea N_l = número de partícula en el estado l del sistema S

N_α = número de partículas en el estado α del sistema R.

Tendremos $E_l + E_\alpha = E$, $N_l + N_\alpha = N$

Si E_l y N_l están fijos, el número de estados accesibles es igual al número de estados accesibles del sistema R accesibles en estas condiciones:

$$\Omega_R(E_\Omega, N_\alpha) = \Omega_R(E - E_l, N - N_l)$$

La probabilidad P_l de observar un estado l es:

$$P_l = \frac{\Omega_R(E - E_l, N - N_l)}{\sum_l \Omega_R(E - E_l, N - N_l)}$$

Podemos hacer un desarrollo de primer orden:

$$\Omega_R(E - E_l, N - N_l) = \exp \frac{S_R(E - E_l, N - N_l)}{k_B}$$

con

$$S_{(R)}(E - E_l, N - N_l) = S_{(R)}(E, N) - \left(\frac{\partial S}{\partial E}\right)_N E_l - \left(\frac{\partial S}{\partial N}\right)_E N_l$$

(II.1.79)

considerando

$$\left(\frac{\partial S}{\partial E}\right)_N = \frac{1}{T} \quad (\text{II.1.80})$$

T temperatura del reservoir

$$\left(\frac{\partial S}{\partial N}\right)_E = -\frac{\mu}{T} \quad (\text{II.1.81})$$

 μ el potencial químico del reservoir

$$\Omega_{(\mathcal{R})}(E - E_\ell, N - N_\ell) = \exp \frac{S_{(\mathcal{R})}(E, N)}{k_B} \times \exp \left[\frac{-E_\ell + \mu N_\ell}{k_B T} \right] \quad (\text{II.1.82})$$

La probabilidad de que el sistema S se encuentre en el estado ℓ es:

$$P_\ell = \frac{\exp \left[\frac{-E_\ell + \mu N_\ell}{k_B T} \right]}{\sum_\ell \exp \left[\frac{-E_\ell + \mu N_\ell}{k_B T} \right]} \quad (\text{II.1.83})$$

distribution grand-canonique.

Se llama Gran Función de partición a la suma:

$$\Xi = \sum_\ell \exp \left[\frac{-E_\ell + \mu N_\ell}{k_B T} \right]$$

 ℓ es un índice general que representa todos los estados posibles del sistema.Si N_ℓ es fijo puede reescribir

$$e^{\frac{\mu N_\ell}{k_B T}} \sum_\ell e^{-\frac{E_\ell}{k_B T}} = Z(N_\ell, T) e^{\frac{\mu N_\ell}{k_B T}} \quad (\text{II.1.85})$$

Y por tanto la Gran función de partición está relacionada con la función de partición canónica por:

$$\Xi(\mu, T) = \sum_{N_\ell=0}^N Z(N_\ell, T) e^{\frac{\mu N_\ell}{k_B T}} \quad (\text{II.1.86})$$

donde $Z(N_l, T)$ es la función de partición correspondiente al número de partículas N_l .

GRAN FUNCIÓN DE PARTICIÓN Y FUNCIONES TERMODINÁMICAS

Número promedio de partículas

$$\bar{N} = \sum_{\ell} N_{\ell} P_{\ell} \quad (\text{II.1.87})$$

ó

$$\bar{N} = \sum_{\ell} \frac{N_{\ell} e^{-\beta(E_{\ell} - \mu N_{\ell})}}{\Xi} \quad (\text{II.1.88})$$

$$\bar{N} = \frac{1}{\beta} \left(\frac{\partial \ln \Xi}{\partial \mu} \right)_T \quad (\text{II.1.89})$$

se obtiene la energía promedio buscando la media de $(E_{\ell} - \mu N_{\ell})$:

$$\bar{E} - \mu \bar{N} = \sum_{\ell} (E_{\ell} - \mu N_{\ell}) P_{\ell} \quad (\text{II.1.90})$$

$$\bar{E} - \mu \bar{N} = \frac{1}{\Xi} \sum_{\ell} (E_{\ell} - \mu N_{\ell}) e^{-\beta(E_{\ell} - \mu N_{\ell})} \quad (\text{II.1.91})$$

se obtiene:

$$\bar{E} - \mu \bar{N} = - \left(\frac{\partial \ln \Xi}{\partial \beta} \right)_{\mu} = k_B T^2 \left(\frac{\partial \ln \Xi}{\partial T} \right)_{\mu} \quad (\text{II.1.92})$$

de donde,

$$\bar{E} = - \left(\frac{\partial \ln \Xi}{\partial \beta} \right)_{\mu} + \frac{\mu}{\beta} \left(\frac{\partial \ln \Xi}{\partial \mu} \right)_{\beta} \quad (\text{II.1.93})$$

La Gran función de partición se puede escribir como:

$$\Xi = Z(T) \exp \left(\frac{\mu N(S)}{k_B T} \right) \quad (\text{II.1.95})$$

$$\ln \Xi = \ln Z + \beta \mu N(S) \quad (\text{II.1.96})$$

La expresión para la entropía del sistema:

$$S = -k_B \sum_{\ell} P_{\ell} \ln P_{\ell}$$

$$S = -k_B \sum_{\ell} \frac{e^{-\beta(E_{\ell} - \mu N_{\ell})}}{\Xi} [-\beta(E_{\ell} - \mu N_{\ell}) - \ln \Xi] \quad (\text{II.1.98})$$

$$S = \frac{1}{T} \sum_{\ell} (E_{\ell} - \mu N_{\ell}) \frac{e^{-\beta(E_{\ell} - \mu N_{\ell})}}{\Xi} + k_B \frac{\sum_{\ell} e^{-\beta(E_{\ell} - \mu N_{\ell})}}{\Xi} \ln \Xi \quad (\text{II.1.99})$$

finalmente,

$$S = \frac{1}{T} (\bar{E} - \mu \bar{N}) + k_B \ln \Xi \quad (\text{II.1.100})$$

Y utilizando (92) obtenemos:

$$S = k_B \left[T \left(\frac{\partial \ln \Xi}{\partial T} \right)_{\mu} + \ln \Xi \right] \quad (\text{II.1.101})$$

$$S = k_B \left[\frac{\partial (T \ln \Xi)}{\partial T} \right]_{\mu} \quad (\text{II.1.102})$$

y si el número de partículas es constante, en términos de Z:

$$S = k_B \left[\frac{\partial (T \ln Z)}{\partial T} \right]_N$$

Y en analogía con la expresión para la energía libre, podemos definir una nueva cantidad termodinámica que se llama el Gran Potencial:

$$\boxed{\Psi = -kT \text{Log } \Xi = \Psi(T, V, \mu)}$$

Y dado que,

$$d\Psi = -SdT - PdV - Nd\mu$$

Y que es una función de estado,

$$d\Psi = \left(\frac{\partial\Psi}{\partial T} \right)_{V,\mu} dT + \left(\frac{\partial\Psi}{\partial V} \right)_{T,\mu} dV + \left(\frac{\partial\Psi}{\partial \mu} \right)_{T,V} d\mu$$

Podemos escribir,

$$\boxed{S = - \left(\frac{\partial\Psi}{\partial T} \right)_{V,\mu}, \quad P = - \left(\frac{\partial\Psi}{\partial V} \right)_{T,\mu}, \quad N = - \left(\frac{\partial\Psi}{\partial \mu} \right)_{T,V}}$$

Entonces,

$$P = \langle P \rangle = kT \left(\frac{\partial \text{Log} \Xi}{\partial V} \right)_{T,\mu}$$

$$N = \langle N \rangle = kT \left(\frac{\partial \text{Log} \Xi}{\partial \mu} \right)_{T,V}$$

$$S = \left(\frac{\partial kT \text{Log} \Xi}{\partial T} \right)_{V,\mu}$$

Lo que nos permite de calcular explícitamente la energía:

$$\boxed{E = kT^2 \left(\frac{\partial \text{Log} \Xi}{\partial T} \right)_{V,\mu} + kT\mu \left(\frac{\partial \text{Log} \Xi}{\partial \mu} \right)_{T,V}}$$

1.3 Grand canonical ensemble

The system is then characterized by the following set of variables: the volume V , the temperature T and the chemical potential μ . Let us denote the Hamiltonian \mathcal{H}_N the Hamiltonian of N particles, the grand partition function $\Xi(V, \beta, \mu)$ reads:

$$\Xi(V, \beta, \mu) = \sum_{N=0}^{\infty} \sum_{\alpha_N} \exp(-\beta(\mathcal{H}_N(\alpha_N) - \mu N)) \quad (1.8)$$

where $\beta = 1/k_B T$ (k_B is the Boltzmann constant) and the sum run over all configurations of N particles and over all configurations for systems having a number of particles going from 0 to *infy*. The grand potential is equal to

$$\beta\Omega(V, \beta, \mu) = -\ln(\Xi(V, \beta, \mu)) \quad (1.9)$$

In a similar way, one defines the probability (distribution) $P(V, \beta, \mu; \alpha_N)$ of having a configuration α_N (with N particles) by the relation

$$p(V, \beta, \mu; \alpha_N) = \frac{\exp(-\beta(\mathcal{H}_N(\alpha_N) - \mu N))}{\Xi(V, \beta, \mu)} \quad (1.10)$$

The derivatives of the grand potential can be expressed as moments of the probability distribution

- Mean number

$$\langle N(V, \beta, \mu) \rangle = -\frac{\partial(\beta\Omega(V, \beta, \mu))}{\partial(\beta\mu)} = \sum_N \sum_{\alpha_N} p(V, \beta, \mu; \alpha_N) \quad (1.11)$$
