4.7: The Grand Canonical Ensemble

Grand as in the French “big” rather than as in the English “magnificent”. This ensemble is “bigger” than the canonical ensemble in that there are more possible microstates.

Summary

The grand canonical ensemble for a pure classical monatomic fluid:

The probability that the system has N particles and is in the microstate Γ_N is proportional to

$$e^{-\beta(H(\Gamma_N)-\mu N)}, \tag{4.7.1}$$

where

$$\beta = \frac{1}{k_B T}. \tag{4.7.2}$$

Writing out all the normalizations correctly gives: the probability that the system has N particles and is in some microstate within the phase space volume element $d\Gamma_N$ about Γ_N is

$$\frac{e^{-\beta(H(\Gamma_N)-\mu N)}}{N! h_0^{3N} \Xi(\beta, V, \mu)} d\Gamma_N, \tag{4.7.3}$$

where the "grand canonical partition function" is

$$\Xi(\beta, V, \mu) = \sum_{N=0}^{\infty} \frac{1}{N! h_0^{3N}} \int e^{-\beta(H(\Gamma_N)-\mu N)} d\Gamma_N \tag{4.7.4}$$

$$= \sum_{N=0}^{\infty} e^{\beta\mu N} Z(\beta, V, N). \tag{4.7.5}$$

This sum is expected to converge when μ is negative.

The connection to thermodynamics is that

$$\Pi(T, V, \mu) = -p(T, \mu)V = -k_B T \ln \Xi(T, V, \mu). \tag{4.7.6}$$