G MACROCANONICAL ENSEMBLE

G.1 *Macrocanonical ensemble*

Similar to the case of the Gibbs-enthalpy and the extension of the canonical potential by an additional Boltzmann-like factor $\exp(pV/(k_B T))$ one could construct a new partition with an associated thermodynamical potential for the case where temperature and volume are controlled, but the particle number is allowed to fluctuate by exchange with a particle reservoir, in analogy to the thermostat regulating the temperature. The ease at which new particles are added to the system is regulated by the chemical potential μ, and the resulting ensemble is called macrocanonical or grand canonical ensemble.

The combined phase space volume of the two systems is given by

$$\omega^* \delta E = \int\limits_{E \leq \mathcal{H} \leq E + \delta E} \prod_i d^3 p_i d^3 q_i = \int\limits_{0 \leq E_1 \leq E} \omega_1^*(E_1, N_1)\omega_2^*(E - E_1, N - N_1) dE_1 \delta E \quad (G.293)$$

If the systems are separated, one would put N_1 particles in the first system but let the energy fluctuate such that the temperature is controlled: That would define the canonical partition.

If now the barrier between the systems is openend there can be an exchange of particles. There is a number of

$$\frac{N!}{N_1!(N - N_1)!} = \binom{N}{N_1} \quad (G.294)$$

possibilities to select N_1 particles from $N = N_1 + N_2$ to be in the first system, implying

$$\omega^*(E, N)\delta E = \int \sum_{N_1} \binom{N}{N_1} \omega_1^*(E_1, N_1)\omega_2^*(E - E_1, N - N_1) dE_1 \delta E \quad (G.295)$$

The binomial factor separates magically into exactly the Gibbs-factors that are needed for each term:

$$\frac{\omega^*(E, N)\delta E}{N! h^{3N}} = \sum_{N_1} \int \frac{\omega_1^*(E_1, N_1)}{N_1! h^{3N_1}} \frac{\omega_2^*(E - E_1, N - N_1)}{(N - N_1)! h^{3(N - N_1)}} dE_1 \delta E \quad (G.296)$$

and with the proper definition of Gibbs-corrected phase space volumes, including the powers of $h^{3N} = h^{3N_1} \times h^{3N_2}$,

$$\omega(E, N)\delta E = \sum_{N_1} \int \omega_1(E, N_1)\omega_2(E - E_1, N - N_1) dE_1 \delta E \quad (G.297)$$

The probability of finding the system in a state characterised by E_1 and N_1 is then given by

$$W(E_1, N_1) dE_1 \sim \omega_1(E_1, N_1)\omega_2(E - E_1, N - N_1) dE_1 \quad (G.298)$$

from which we continue as before by expanding the logarithm of ω_2 around the maximum of W

$$\ln \omega_2(E - E_1, N - N_1) = \ln \omega_2(E, V) - \underbrace{\frac{\partial \omega_2}{\partial E}}_{=\frac{1}{k_B T}=\beta} E_1 - \underbrace{\frac{\partial \ln \omega_2}{\partial N}}_{=\frac{\mu}{k_B T}=\ln z} N_1 \tag{G.299}$$

from $S = k_B \ln \omega$ such that $\frac{\partial S}{\partial E} = \frac{1}{k_B T}$ and $\frac{\partial S}{\partial N} = \frac{\mu}{k_B T}$. With the definition of fugacity

$$\ln z = \frac{\mu}{k_B T} \quad \rightarrow \quad z = \exp\left(\frac{\mu}{k_B T}\right) \tag{G.300}$$

as the chemical potential in units of the thermal energy in analogy to the inverse temperature $\beta = \frac{1}{k_B T}$ we find for the probability

$$W(E_1, N_1)dE_1 \sim \omega(E_1, V_1, N_1) \exp\left(-\frac{E_1 - \mu N}{k_B T}\right) dE_1 \tag{G.301}$$

such that the fugacity plays the role of an analogous Boltzmann-factor to introduce the replacement of N by μ.

G.2 *Macrocanonical potential* J *and macrocanonical partition* $\mathcal{Z}$

The associated thermodynamical potential to the macrocanonical partition $\mathcal{Z}$ is the macrocanonical potential J, naturally as a function of the state variables T, V and μ, the latter replacing N:

$$J(T, V, \mu) = -k_B T \ln \mathcal{Z} \tag{G.302}$$

as the logarithm of the macrocanonical partition $\mathcal{Z}$

$$\mathcal{Z} = \sum_N \int_E dE\, \omega(E, V, N) \exp\left(-\frac{E - \mu N}{k_B T}\right) \tag{G.303}$$

Derivatives of the macrocanonical potential J with respect to T, V and μ are then linked to entropy S, pressure p and particle number N, respectively.

G.3 *Chemical potential* μ *and fugacity* z

A fun example for a canonical, discrete system is a microscopic model for a polymer, i.e. an elastic string: We'll set up a canonical partition and extend it to a macrocanonical partition in order to get some intuition about the chemical potential and the associated fugacity. Let's assume that the string is a chain of N monomers which can be in two configurations, the long configuration with length a and the short configuration with length b. The string is kept under tension σ, such that there is mechanical work σdl performed, if the the length l of the chain is changed, in analogy to the work performed by pressure $p dV$.

As in this system the state variables T, σ and N are controlled, we chose the enthalpy $G(T, \sigma, N)$ as the thermodynamical potential, with the associated canonical partition $Z_G(T, p, N)$:

$$Z_G = \sum_i \binom{N}{i} \exp\left(-\frac{\sigma l(i)}{k_B T}\right) =$$

$$\sum_i \binom{N}{i} \exp\left(-\frac{\sigma}{k_B T}[ia + (N-i)b]\right) = \left[\exp\left(-\frac{a\sigma}{k_B T}\right) + \exp\left(-\frac{b\sigma}{k_B T}\right)\right]^N \tag{G.304}$$

with a factorising partition sum, $Z_G T, \sigma, N = Z_G(T, \sigma, 1)^N$. Clearly, the length of the polymer chain $l(i)$ depends on the number i of long elements a and the number $N - i$ of short elements b. The combinatorial factor $\binom{N}{i} = N!/i!/(N-i)!$ counts the number of possibilities to distribution i long elements in a chain of N elements in total.

Then, he Gibbs-enthalpy then follows from the canonical partition as

$$G(T, \sigma) = -k_B T \ln Z_G = \sigma l - TS \tag{G.305}$$

with the corresponding differential dG,

$$dG = -S dT + l d\sigma \tag{G.306}$$

such that the length of the chain at fixed tension and temperature is given by

$$l = \frac{\partial G}{\partial \sigma} = N \frac{a \exp\left(-\frac{a\sigma}{k_B T}\right) + b \exp\left(-\frac{b\sigma}{k_B T}\right)}{\exp\left(-\frac{a\sigma}{k_B T}\right) + \exp\left(-\frac{b\sigma}{k_B T}\right)} \tag{G.307}$$

in thermodynamical equilibrium: Immediately, one would interpret eqn. (G.307) as a weighted sum of $N \exp(-a\sigma/(k_B T))$ monomers in the a-configuration and of $N \exp(-b\sigma/(k_B T))$ monomers in the b-configuration, to form the expectation value for the total length l. In complete analogy, differentiation with respect to temperature yields the entropy, $S = -\frac{\partial G}{\partial T}$.

Figs. 16 and 17 show the equation of state, i.e. the relation between tension σ, length l and temperature T for this model, and compare the analytic solution derived from Z_G with the expectation values of samples drawn from the canonical ensemble my means of a Monte-Carlo Markov-chain method, namely, the Metropolis-Hastings algorithm. Perhaps a bit surprisingly, the polymer chain in fact contracts at fixed tension with increasing temperature, as the Boltzmann-probability for replacing a long monomer with a short one increases. And there is, at least for small tensions, a linear relationship between length and force reminiscent of Hooke's law. Only for large tensions, when the chain is almost fully elongated, the curve is significantly steeper, as there are fewer configurations consistent with increasing length.

We can extend the idea of a polymer chain to include a chemical potential μ: The polymer chain could be in a solution of monomers, which can leave the solution and be built into the polymer chain, controlled by the parameter μ.

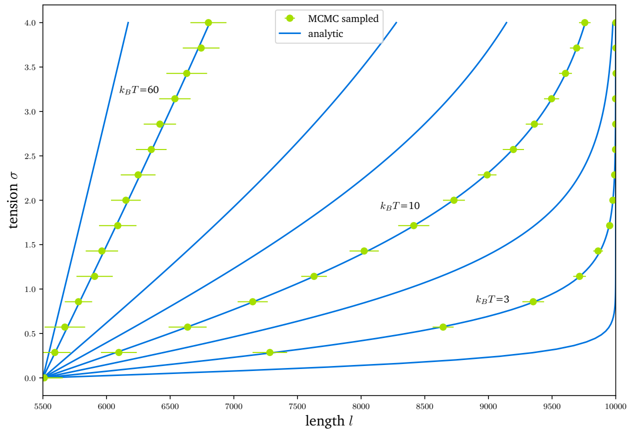

Figure 16: Relation between tension σ and length l of the rubber band, parameterised by temperature $k_B T$, as it would result from the partition sum Z_G and with the most likely value and its dispersion as determined numerically with a Metropolis-Hastings-algorithm for sampling from the canonical ensemble (reference: bachelor-thesis M. Kretschmer)

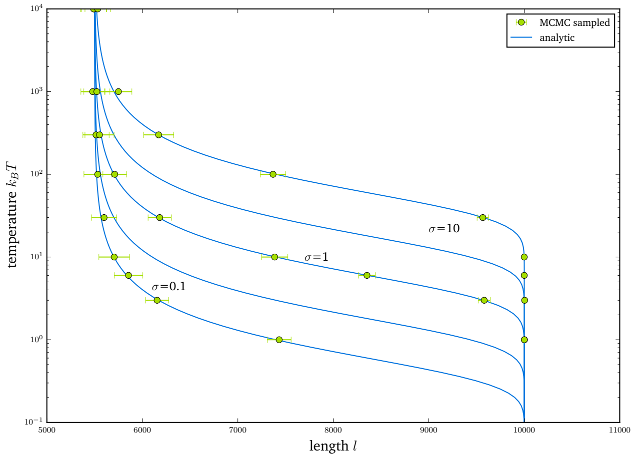

Figure 17: Relation between temperature $k_B T$ and length l of the rubber band, parameterised by tension σ, as it would result from the partition sum Z_G and with the most likely value and its dispersion (reference: bachelor-thesis M. Kretschmer)

For the corresponding macrocanonical partition we need the Gibbs-factor $\frac{1}{j!}$, the canonical partition $Z(T, \sigma, j)$ now as a function of l and a weighting with fugacity:

$$\mathcal{Z}(T, \sigma, \mu) = \sum_j \frac{1}{j!} \left[\sum_i^j \binom{j}{i} \exp\left(-\frac{\sigma l(i)}{k_B T}\right) \right] \exp\left(\frac{\mu j}{k_B T}\right) \tag{G.308}$$

such that the macrocanonical potential $J(T, \sigma, \mu)$ is given by

$$J(T, \sigma, \mu) = -k_B T \ln \mathcal{Z}(T, \sigma, \mu) \tag{G.309}$$

with corresponding derivatives

$$\frac{\partial J}{\partial T} = -S, \quad \frac{\partial J}{\partial l} = -\sigma, \quad \frac{\partial J}{\partial \mu} = -N \tag{G.310}$$

The canonical partition sum factorises, $Z(T, \sigma, N) = Z(T, \sigma, 1)^N$ into powers of the canonical partition of a single chain link,

$$Z(T, \sigma, 1) = \exp\left(-\frac{a\sigma}{k_B T}\right) + \exp\left(-\frac{b\sigma}{k_B T}\right) \tag{G.311}$$

Collecting all results then yields for the macrocanonical partition

$$\mathcal{Z}(T, \sigma, \mu) = \sum_j \frac{1}{j!} Z(T, \sigma, 1)^j \exp\left(\frac{\mu}{k_B T}\right)^j = \\ \sum_j \frac{1}{j!} \left[Z(T, \sigma, 1) \exp\left(\frac{\mu}{k_B T}\right) \right]^j = \exp\left(\exp\left(\frac{\mu}{k_B T}\right) Z(T, \sigma, 1) \right) \tag{G.312}$$

where the double exponential is typical for the structure of the macrocanonical partition sum $\mathcal{Z}$. For this case, S, l and N can be computed by differentiating $J = -k_B T \ln \mathcal{Z}$. It is a funny side effect that by providing a high chemical potential μ and pulling on the string with σ the system assembles the chain spontaneously! There is an inconsistency though, which does not invalidate the macrocanonical ensemble: To have a partition function that depends entirely on intensive variables is at odds with the Gibbs-Duhem relation, which disallows all intensive state variables in the potential for making statements about extensive state variables, as all information of the system is lost.

We have seen how the macrocanonical partition is assembled from fugacity-weighted canonical partitions, but can this process be inverted? It is possible to recover the canonical partition Z from the macrocanonical partition $\mathcal{Z}$. Their relation is given by

$$\mathcal{Z}(T, V, \mu) = \sum_N \exp\left(\frac{\mu}{k_B T}\right)^N Z(T, V, N) \tag{G.313}$$

as a fugacity-weighted summation over the canonical partition.

In turn, it factorises

$$Z(T,V,N) = \frac{1}{N!} Z(T,V,1)^N \tag{G.314}$$

into powers over the canonical partition pertaining to a single particle, N = 1. Introducing the fugacity explicitly,

$$\mathcal{Z}(T,V,z) = \sum_N Z(T,V,N) z^N = \sum_N \frac{1}{N!} \left(z\, Z(T,V,N)\right)^N \tag{G.315}$$

with $z = \exp\left(\frac{\mu}{k_B T}\right)$ shows that $\mathcal{Z}$ is in fact a power series in z with the canonical partition as prefactors. The variable for the fugacity is already aptly named: When performing an analytic continuation of $\mathcal{Z}$ from real-valued z to complex-valued z, the series becomes a Laurent series. Then, the canonical partition is obtained through complex differentiation

$$Z(T,V,N) = \left.\frac{d^N}{dz^N} \mathcal{Z}(T,V,z)\right|_{z=0} \tag{G.316}$$

where the N-fold differentiation can be rewritten as a complex integration around a loop at $z = 0$

$$Z(T,V,N) = \frac{1}{2\pi i} \oint \frac{\mathcal{Z}(T,V,z)}{z^{N+1}} \tag{G.317}$$

which can be evaluated using the tools of complex analysis, i.e. the residue theorem.