Coupled Harmonic Oscillators

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1 Conclusions [1]

1.1 Question 3

From our simulation experiment in question 3, it follows that the probability distribution for a given state k of a single harmonic oscillator reads:

$$P(k) = \frac{\exp[-\beta E_k]}{q} \tag{1}$$

with constants β and q. In statistical thermodynamics the numerator $\exp[-\beta E_k]$ is called the Boltzmann factor. The constant q is called the molecular partition function or molecular partition sum, defined as the sum of Boltzmann factors over all states of the oscillator.

$$q = \sum_{k=0}^{\infty} \exp[-\beta E_k] \tag{2}$$

Substituting $x = \exp(-\beta\hbar\omega)$ we can rewrite the partition sum of q of a harmonic oscillator as a geometric series employing:

$$\sum_{i=0}^{\infty} x^i = \frac{1}{1-x} \quad \text{for} \quad |x| < 1 \tag{3}$$

thus:

$$q = \frac{1}{1 - \exp[-\beta E_k]} \tag{4}$$

The average energy $\langle E_i \rangle$ of a single oscillator can be related to β using the same substitution as in eq. (3) and employing :

$$\sum_{i=0}^{\infty} i x^i = \frac{x}{(1-x)^2} \quad \text{for} \quad |x| < 1 \tag{5}$$

which is eq (3) diferentiated with respect to x and multiplied by x, leads to the following relation:

$$\langle E_i \rangle = \sum_{k=0}^{\infty} \hbar\omega k P(k) = \hbar\omega \frac{\sum_{k=0}^{\infty} k \exp[-\beta\hbar\omega k]}{\sum_{k=0}^{\infty} \exp[-\beta\hbar\omega k]} = \frac{\hbar\omega}{\exp[-\beta\hbar\omega] - 1} \tag{6}$$

The latter means that for big enough number of oscillators, a single oscillator i is surrounded by a "heath bath". The temperature follows from the total energy E, which in turn determines $\langle E_i \rangle$ and β.Thus, from the average energy $\langle E_i \rangle$ and the relation $\beta = 1/k_B T$ we can estimate the temperature of the simulated system.

1. For a number of system energies (E_t) use simulation data to find $\langle E_i \rangle$ and β. Check your results with eq. (6)

1.2 Question 4

From our simulation experiment in question 4, it follows that the entropy increase in time ands reaches maximum value when we start from the less likely distribution.

References

[1] Thijs J.H. Vlugt, Jan P.J.M. van der Eerden, Marjolein Dijkstra, Berend Smit, and Daan Frenkel. *Introduction to Molecular Simulation and Statistical Thermodynamics.* Delft, The Netherlands, 2008.