AstroParis graduate program
Master 1st year - "Space Science and Technology"
Observatoire de Paris - PSL

Statistical Physics

François Levrier
Guillaume Dréau
Raphaël Duque
Aurélien Pascal

Homework assignment 3 - Correction

November 25th, 2020

I - On the origin of elasticity in materials

We seek to understand the origin of elasticity, a phenomenon by which materials that are deformed by external systems exert forces to return to their equilibrium shape.

A one-dimensional microscopic model for elasticity

We consider a one-dimensional chain of $N+1$ atoms linked by N bonds of constant length l. We suppose the number of atoms is very large. The bonds can point either to the right (in which case the next atom is a distance l to the right of the preceding atom) or to the left (the converse). The first atom of the chain is fixed to the origin, and the end of the chain is free. We characterize each configuration of the chain bonds by the algebraic distance L (that is, the difference in coordinates) between the first and the last atom. For example, with $N+1=4$ atoms, the microstate with successive bond directions (right, right, left) will have atoms on coordinates $(0, l, 2l, l)$ from first to last, and thus $L = l$.

1. For a given macrostate L, how many chain configurations $\Omega(L)$ are there ?

Solution

We denote by n the number of bonds pointing to the right. The $N-n$ other bonds point to the left. The number of configurations of the chains corresponding to macrostate with total length L is :

$$\Omega(L) = \binom{N}{n} = \frac{N!}{n!(N-n)!} \tag{1.1}$$

Simple combinatronics show that $L/l = 2n - N$.

2. Deduce the entropy of state L.

Solution

By definition, the entropy of this state is $S = k_B \ln \Omega(L)$.

3. The energy of the chain does not depend on the configuration of the bonds, and the chain can therefore store no energy. In which state L_0 are we most likely to find the chain ? How would you geometrically characterize this equilibrium state ? We recall the Stirling formula $\ln N! \sim_{N\to\infty} N \ln N + o(N \ln N)$.

SOLUTION

The chain's energy is independent of the bond configuration, therefore all of its microstates are equiprobable. Therefore, the chain will occupy the macrostate with largest number of microstates. In other words, with largest entropy. S is maximized for $n = N/2$, in which case one has $L_0 = 0$ and :

$$S(L=0) = k_B \ln \binom{N}{N/2} \tag{1.2}$$

$$= k_B \left(\ln N! - 2 \ln \frac{N}{2}! \right) \tag{1.3}$$

$$\sim_{N\to\infty} k_B \left[N \ln N - 2\frac{N}{2} \ln \frac{N}{2} \right] \tag{1.4}$$

$$= k_B N \ln 2 \tag{1.5}$$

This state is geometrically "collapsed" or "tangled". It is the one in which the chain occupies the smallest volume.

We now consider the chain immersed in a heat bath at temperature T. An external operator uses a micro-manipulation device to exert a force F_{op} on the end of the chain. The other end remains fixed at the origin. This manipulation results in the chain changing in length from its initial state L_0 by a small quantity δL.

4. Write the first law of thermodynamics for the chain in this transformation. With which system(s) did the chain exchange energy ?

SOLUTION

The first law of thermodynamics on the chain writes :

$$\delta U_{\text{chain}} = \delta Q + \delta W = 0 \tag{1.6}$$

as the chain can store no energy.

$\delta W = F_{\text{op}} \delta L$ is the work done on the chain by the operator and δQ is the heat transferred to the chain. This heat is provided to the chain by the heat bath.

5. We now consider the heat bath as a system. What is the change in its internal energy δU_{HB} after the transformation ? Link this quantity to the corresponding displacement δL. A priori, what are the possible values for δL ?

SOLUTION

Upon the operator's action, the heat bath transfers $\delta Q = -\delta W$ to the chain, and therefore its internal energy changed by $\delta U_{\mathrm{HB}} = -\delta Q = \delta W = F_{\mathrm{op}} \delta L$. We do not know the exact mechanics of the chain. Therefore, the operator's action can result in any response from the chain, and δL can assume any value from $-Nl$ to Nl.

6. We seek to calculate the state of the heat bath and chain after the operator's action. Write the partition function for the heat bath after the transformation and deduce the average change in energy $\overline{\delta U_{\mathrm{HB}}}$ of the heat bath during the transformation. On average, did the heat bath gain or lose energy ? Deduce the average extension $\overline{\delta L}$ of the chain. We denote $R_{\mathrm{M}} = Nl$ the maximum length of the chain.

SOLUTION

The partition function for the heat bath is :

$$
\begin{aligned}
Z_{\mathrm{HB}} &= \sum_{\delta L=-Nl}^{Nl} e^{-\beta \delta U_{\mathrm{HB}}} \Omega(\delta L) && (1.7) \\
&= \sum_{\delta L=-Nl}^{Nl} e^{-\beta F_{\mathrm{op}} \delta L} \Omega(\delta L) && (1.8)
\end{aligned}
$$

We change variables by summing on the number of bonds pointing to the right n :

$$
\begin{aligned}
Z_{\mathrm{HB}} &= \sum_{n=0}^{N} e^{-\beta F_{\mathrm{op}}(2n-N)l} \binom{N}{n} && (1.9) \\
&= e^{\beta F_{\mathrm{op}} Nl} \sum_{n=0}^{N} \binom{N}{n} e^{-2\beta F_{\mathrm{op}} nl} && (1.10) \\
&= e^{\beta F_{\mathrm{op}} Nl} \left(1 + e^{-2F_{\mathrm{op}} l \beta}\right)^{N} && (1.11)
\end{aligned}
$$

The average energy of the heat bath is :

$$
\begin{aligned}
\overline{\delta U_{\text{HB}}} &= -\frac{\partial \ln Z_{\text{HB}}}{\partial \beta} && (1.12)\\
&= -F_{\text{op}} l N + 2F_{\text{op}} l N \frac{e^{-2\beta F_{\text{op}} l}}{1+e^{-2\beta F_{\text{op}} l}} && (1.13)\\
&= F_{\text{op}} l N \left(\frac{e^{-2\beta F_{\text{op}} l}-1}{e^{-2\beta F_{\text{op}} l}+1}\right) && (1.14)\\
&= F_{\text{op}} R_{\text{M}} \tanh \beta F_{\text{op}} l && (1.15)
\end{aligned}
$$

On average, the heat bath gained energy. Indeed, the operator provides energy through work to the chain, which cannot store the energy. Therefore, the heat bath takes on this energy.

The average extension of the chain will thus be :

$$\overline{\delta L} = \frac{\overline{\delta U_{HB}}}{F_{\text{op}}} = R_{\text{M}} \tanh \beta F_{\text{op}} l \tag{1.16}$$

7. Show that the chain exhibits elastic behavior. What is its stiffness K ? Is the chain more or less stiff at higher temperatures ?

SOLUTION

After operation, the chain is at equilibrium and therefore exerts a recoil force F_e on the operator, which is :

$$F_e = -F_{\text{op}} \tag{1.17}$$

For small extensions $\delta L \ll R_{\text{M}}$, we can use $\tanh x \sim_{x\to 0} x + o(x)$ to obtain :

$$F_e = -\frac{1}{\beta R_{\text{M}} l}\delta L \tag{1.18}$$

The chain therefore behaves like an elastic material of stiffness $K = 1/R_{\text{M}}\beta l = k_B T/Nl^2$.

8. Discuss in what way the origin of the elastic force can be dubbed as "thermodynamical". In this picture, does this force derive from a fundamental interaction ?

SOLUTION

As the operator pulls on the chain, the heat bath takes on all the energy provided by the operator, as the chain cannot store energy. The more the operator pulls, the higher the energy the heat bath must assume, which puts the heat bath in less and less likely states (more and more suppression by the Boltzmann factor).

To allow the heat bath to return to the initial low energy state, the chain exerts an "elastic force" on the operator. This force however is purely thermodynamical, and not based on a fundamental interaction like the electric or gravitational forces are.

The entropic origin of the elastic forces

We seek a more profound explanation to the elastic force.

9. We consider a macrostate in which the chain has small length $\delta L \ll R_{\mathrm{M}}$. What is the expression of the entropy of this macrostate ? We advise to introduce $\delta n = \delta L/l \ll N$.

SOLUTION

In this state, the number of bonds pointing to the right is $(N + \delta n)/2$, with $\delta n = \delta L/l \ll N$.

The entropy of this macrostate is therefore :

$$S(\delta L) = k_B \ln \binom{N}{\frac{N+\delta n}{2}} \tag{1.19}$$

$$= k_B \ln \frac{N!}{\left(\frac{N+\delta n}{2}\right)! \left(\frac{N-\delta n}{2}\right)!} \tag{1.20}$$

Using Stirling's formula above for large N, we have :

$$S(\delta L)/k_B = N \ln N - \left(\frac{N+\delta n}{2} \ln \frac{n+\delta n}{2} + \frac{N-\delta n}{2} \ln \frac{N-\delta n}{2} \right) \tag{1.21}$$

10. Develop $S(\delta L)$ to the lowest order that still depends on $\delta n/N$.

SOLUTION

Now we separate the logarithms as such :

$$\frac{N \pm \delta n}{2} \ln \frac{N \pm \delta n}{2} = \frac{N \pm \delta n}{2} \left(\ln \frac{N}{2} + \ln \left(1 \pm \frac{\delta n}{N} \right) \right) \tag{1.22}$$

$$= \frac{N}{2} \ln \frac{N}{2} + \frac{N}{2} \ln \left(1 \pm \frac{\delta n}{N} \right) \tag{1.23}$$

$$\pm \frac{\delta n}{2} \ln \frac{N}{2} \pm \frac{\delta n}{2} \ln \left(1 \pm \frac{\delta n}{N} \right) \tag{1.24}$$

We now develop the logarithms in $\delta n/N \ll 1$:

$$\ln(1 \pm \delta n/N) \sim \pm\delta n/N \tag{1.25}$$

Reinjecting in the above equation, the linear terms vanish and we finally obtain :

$$S(\delta L) = k_B N \ln 2 - k_B \frac{\delta n^2}{N} \tag{1.26}$$

11. Express δS, the difference in entropies between state δL and the equilibrium state, as a function of δL. Express the elastic F_e force as a function of δS and δL.

SOLUTION

Thus, the difference of entropies between the state δL and the equilibrium state is :

$$\begin{aligned} \delta S &= -k_B \frac{\delta n^2}{N} && (1.27)\\ &= -k_B \frac{\delta L^2}{N l^2} && (1.28)\\ & && (1.29) \end{aligned}$$

Finally, the recoil force of the chain is :

$$\begin{aligned} F_e &= -K\delta L && (1.30)\\ &= -K\frac{Nl^2}{k_B}\left(-\frac{\delta S}{\delta L}\right) && (1.31)\\ &= T\frac{\delta S}{\delta L} && (1.32) \end{aligned}$$

12. Why can it be said that this elastic force is "entropic" ?

SOLUTION

Therefore, if we introduce the potential entropy field $S_p(x)$, equal to the entropy of the chain if its end were displaced to x, then the recoil force can be seen as deriving from this potential and seeking to increase the entropy of the system, with a proportionality factor linear in temperature :

$$F_e(x) \propto T\nabla S_p(x) \tag{1.33}$$

Such forces are called entropic forces, and are purely thermodynamical phenomena. They do not derive from a fundamental interaction.

13. Do you know of other entropic forces ? Think of macroscopic forces exerted by systems of non-interacting particles.

$\boxed{\text{SOLUTION}}$

Another example are pressure forces. Consider a classical ideal gas in a box of section Σ and variable length x. Its volume is $V(x) = \Sigma x$. As per the Sackur-Tetrode equation, the entropy $S(x)$ of the gas equals $Nk_B \ln V(x)$ up to a constant.

The pressure force exerted on the internal surface of the box is :

$$F_p = P\Sigma = \frac{NkT}{V}\Sigma \tag{1.34}$$

where we used the ideal gas equation of state $PV = NkT$.
In addition, we have :

$$\begin{aligned} \frac{\partial S}{\partial x} &= \frac{\partial S}{\partial V}\frac{\partial V}{\partial x} && (1.35) \\ &= \frac{Nk_B}{V}\Sigma && (1.36) \end{aligned}$$

Therefore, the pressure force is $F_p = T\partial S/\partial x$, and is an entropic force.

One direction of contemporary theoretical physics is to formulate gravitation as an entropic phenomenon. The term "emerging phenomenon" is also common.