Random walk: One dimensional chain problem

Masatsugu Sei Suzuki
Department of Physics, SUNY at Binghamton

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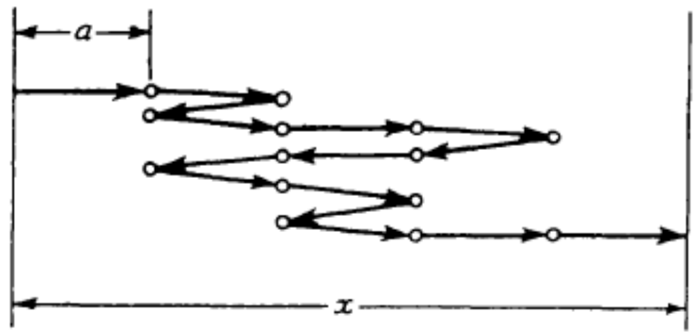
The chain problem is very helpful for our understanding the approach of the microcanonical ensemble. This problem is discussed in the book of Kubo.



There is a one-dimensional chain consisting of n (>>1) elements, as is seen in the figure. Let the length of each element be a and the distance between the end points x. Find the entropy of this chain as a function of x and obtain the relation between the temperature T of the chain and the force (tension) which is necessary to maintain the distance x, assuming the joints to turn freely.

In order to specify a possible configuration of the chain, we indicate successively, starting from the left end, whether each consecutive element is directed to the right (+) or to the left (-). In the above figure, we have (+ + - + + + - - - + + - + + +). The number of elements n_+ directed to the right and the number n_- of those directed to the left together determine the distance between the ends of the chain x.

$$x = (n_+ - n_-)a$$

$$n = n_+ + n_-$$

$$n_+ = \frac{1}{2}n(1+\frac{x}{na}), \qquad n_- = \frac{1}{2}n(1-\frac{x}{na})$$

The number of configurations having the same x and hence the same n_+, n_- is given by

$$W(x) = \frac{n!}{n_+! n_-!}$$

With the help of the Stirling's approximation, the entropy is obtained as

$$\begin{aligned}
S(x) &= k_B \ln W(x) \\
&= k_B (\ln n! - \ln n_+! - \ln n_-!) \\
&= k_B (n \ln n - n - n_+ \ln n_+ + n_+ - n_- \ln n_- + n_-) \\
&= k_B (n \ln n - n_+ \ln n_+ - n_- \ln n_-) \\
&= n k_B [\ln n - \frac{1}{2}(1 + \frac{x}{na}) \ln \frac{1}{2} n (1 + \frac{x}{na}) - \frac{1}{2}(1 - \frac{x}{na}) \ln \frac{1}{2} n (1 - \frac{x}{na})] \\
&= n k_B [\ln 2 - \frac{1}{2}(1 + \frac{x}{na}) \ln (1 + \frac{x}{na}) - \frac{1}{2}(1 - \frac{x}{na}) \ln (1 - \frac{x}{na})]
\end{aligned}$$

We note that

$$S(x) = n k_B [\ln 2 - \frac{1}{2}(1 + \frac{x}{na}) \ln (1 + \frac{x}{na}) - \frac{1}{2}(1 - \frac{x}{na}) \ln (1 - \frac{x}{na})]$$

$$\begin{aligned}
S'(x) &= \frac{n k_B}{2an} [\ln \left(\frac{an - x}{2a} \right) - \ln \left(\frac{an + x}{2a} \right) \\
&= \frac{k_B}{2a} \ln \left(\frac{an - x}{an + x} \right)
\end{aligned}$$

We note that the energy U is independent of x. The Helmholtz free energy is given by

$$F = U - ST$$

From the relation, $dF = -PdV - SdT$,

$$P = -\left(\frac{\partial F}{\partial V} \right)_T = T \left(\frac{\partial S}{\partial V} \right)_T$$

or

$$X = -\left(\frac{\partial F}{\partial x} \right)_T = T \left(\frac{\partial S}{\partial x} \right)_T$$

The tension X is obtained as

$$X = T\left(\frac{\partial S}{\partial x}\right)_T$$

$$= -\frac{k_B T}{2a}\ln\left(\frac{1+\dfrac{x}{na}}{1-\dfrac{x}{na}}\right)$$

$$= -\frac{k_B T x}{a^2}[1+\frac{1}{3}\left(\frac{x}{na}\right)^2+\frac{1}{5}\left(\frac{x}{na}\right)^5+\frac{1}{7}\left(\frac{x}{na}\right)^7+...]$$

or

$$-\frac{aX}{k_B T} = \frac{1}{2}\ln(\frac{1+\dfrac{x}{na}}{1-\dfrac{x}{na}}) .$$

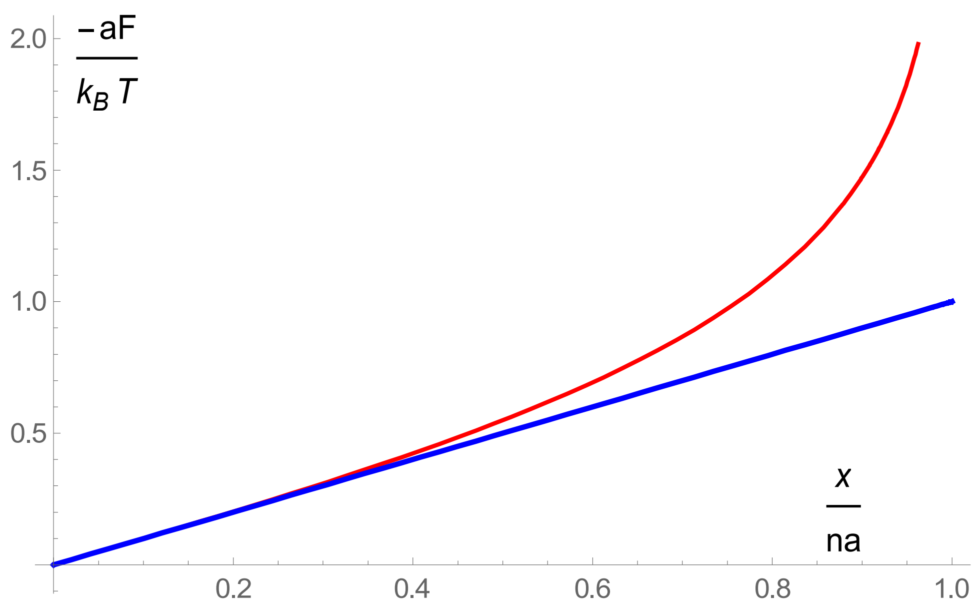


Fig. Normalized force $-\dfrac{aX}{k_B T}$ vs *x*.

The last equality is the expansion formula for $x << na$, and its first term corresponds to Hooke's law. This chain is the simplest model embodying the essential property of rubber elasticity.

REFERENCE

R. Kubo Statistical Mechanics An Advance Courses with Problems and Solutions (North-Holland, 1965).