Equipartition Theorem

In the classical limit, the average of $z\,\partial H/\partial z$, where H is the Hamiltonian and z is a generalized coordinate or a conjugate momentum, can be expressed as a ratio of integrals over phase space:

$$\left\langle z\frac{\partial H}{\partial z}\right\rangle = \int d\omega \left(z\frac{\partial H}{\partial z}\right) e^{-\beta H} \Big/ \int d\omega\, e^{-\beta H}.$$

The phase-space measure can be expressed as $d\omega = d\omega' dz$. The integral over z in the numerator is

$$\int_{z_{\min}}^{z_{\max}} dz\,(z\,\partial H/\partial z)\,e^{-\beta H}$$

A. Express the integrand with a factor of $(\partial/\partial z)e^{-\beta H}$.

$$z\frac{\partial H}{\partial z}e^{-\beta H} = -\frac{1}{\beta} z \frac{\partial}{\partial z} e^{-\beta H}$$

B. Integrate by parts to get a term with integrand $e^{-\beta H}$ and a boundary term.

$$\int_{z_{min}}^{z_{max}} dz\left(-\frac{1}{\beta} z\frac{\partial}{\partial z}e^{-\beta H}\right) = -\frac{1}{\beta} z e^{-\beta H}\Big|_{z_{min}}^{z_{max}} + \frac{1}{\beta}\int_{z_{min}}^{z_{max}} dz\, e^{-\beta H}$$

Show that if H approaches $+\infty$ as z approaches its endpoints, the average reduces to

$H \to +\infty \implies e^{-\beta H} \to 0$

$$\langle z\,\partial H/\partial z\rangle = T,$$

where T is the temperature.

$$\left\langle z\frac{\partial H}{\partial z}\right\rangle = \frac{0 + \frac{1}{\beta}\int d\omega\, e^{-\beta H}}{\int d\omega\, e^{-\beta H}} = \frac{1}{\beta} = T$$

C. Determine the average value of each of the following terms in H:

- H depends on the momentum component p only through the term $p^2/2m$

$$p\frac{\partial}{\partial p}(p^2/2m) = 2\left(\frac{p^2}{2m}\right) \implies 2\left\langle\frac{p^2}{2m}\right\rangle = T \implies \left\langle\frac{p^2}{2m}\right\rangle = \frac{1}{2}T$$

- H depends on the coordinate x only through the term $\frac{1}{4}\gamma x^4$

$$x\frac{\partial}{\partial x}\left(\frac{1}{4}\gamma x^4\right) = 4\left(\frac{1}{4}\gamma x^4\right) \implies 4\left\langle\frac{1}{4}\gamma x^4\right\rangle = T \implies \left\langle\frac{1}{4}\gamma x^4\right\rangle = \frac{1}{4}T$$

- H depends on the the angular momentum component L only through the term $L^2/2I$ (the moment of inertia I is positive)

$$L\frac{\partial}{\partial L}(L^2/2I) = 2(L^2/2I) \implies 2\langle L^2/2I\rangle = T \implies \langle L^2/2I\rangle = \frac{1}{2}T$$

Compare your results with your neighbors.

Show your results to the instructor.

If z is a generalized coordinate or a conjugate momentum, then in the classical limit

$$\left\langle z \frac{\partial H}{\partial z} \right\rangle = T,$$

where T is the temperature.

D. Show that the operator $z\partial/\partial z$ counts the powers of z: $(z\,\partial/\partial z)z^n = n\,z^n$.

$z \frac{\partial}{\partial z} z^n = z \cdot n z^{n-1} = n \cdot z^n$

Determine the average energy U in the classical limit for the following systems:

E. N atoms in a harmonic trapping potential with Hamiltonian

$$H = \sum_{n=1}^{N} \left(\frac{1}{2m}\vec{p}_n^{\,2} + \frac{1}{2}m\omega^2 \vec{r}_n^{\,2} \right).$$

$U = \langle H \rangle = N \cdot (\frac{3}{2}T) + N \cdot (\frac{3}{2}T) = 3NT$

F. N quartic oscillators with Hamiltonian

$$H = \sum_{n=1}^{N} \left(\frac{1}{2m}p_n^2 + \frac{1}{4}\gamma x_n^4 \right).$$

$U = \langle H \rangle = N \cdot (\frac{1}{2}T) + N(\frac{1}{4}T) = \frac{3}{4}NT$

G. an ideal gas of N diatomic molecules with atomic mass m, vibrational frequency ω, and bond length R. Its Hamiltonian can be approximated by

$$H = \sum_{n=1}^{N} \left(\frac{1}{4m}\vec{p}_n^{\,2} + \frac{1}{4}m\omega^2 z_n^2 + \frac{1}{mR^2}\left(L_{nx}^2 + L_{ny}^2\right) \right),$$

where $R + z_n$ is the separation of the two atoms in the molecule and L_{nx} and L_{ny} are components of the internal angular momentum of the molecule.

$U = \langle H \rangle = N(\frac{3}{2}T) + N \cdot (\frac{1}{2}T) + N \cdot (\frac{1}{2}T \cdot 2) = 3NT$

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