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Two Lectures about the Virial Theorem

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Lecture I - Deterministic Virial

I.1 Discrete and Newtonian

- **Ordinary forces**
- **Fluctuating forces**
- **Particle systems**

I.2 Continuum and Eulerian

Main reference: G. Marc and W.G. McMillan, The virial theorem. Adv. Chem. Phys. 58, 209-361 (1985).

I.1 Deterministic Virial, Discrete and Newtonian

Ordinary forces

"The mean *vis viva* [$\equiv$ kinetic energy] of the system is equal to its [force] virial" (Rudolf Clausius, 1870)

$$\boxed{A[\boldsymbol{f}\cdot\boldsymbol{x}] = -2\,A[k],\ \ 2\,k := m\dot{\boldsymbol{x}}\cdot\dot{\boldsymbol{x}}} \quad \Leftarrow \quad \boxed{m\ddot{\boldsymbol{x}} = \boldsymbol{f}\,,\ \ \boldsymbol{x} = x(t) - o}$$

$$m\ddot{\boldsymbol{x}} = \boldsymbol{f} \quad \Rightarrow \quad m\ddot{\boldsymbol{x}} \cdot \boldsymbol{x} = \boldsymbol{f} \cdot \boldsymbol{x} =: \textbf{the } \textbf{\textit{virial}} \textbf{ of force } \boldsymbol{f}.$$

Note that

$$\ddot{\boldsymbol{x}} \cdot \boldsymbol{x} = \begin{cases} \dfrac{d}{dt}(\dot{\boldsymbol{x}} \cdot \boldsymbol{x}) - \dot{\boldsymbol{x}} \cdot \dot{\boldsymbol{x}} \\ \\ \dfrac{1}{2}\dfrac{d^2}{dt^2}(\boldsymbol{x} \cdot \boldsymbol{x}) - \dot{\boldsymbol{x}} \cdot \dot{\boldsymbol{x}} \end{cases}.$$

With a use of upper alternative,

$$\frac{d}{dt}(m\dot{\boldsymbol{x}} \cdot \boldsymbol{x}) - m\dot{\boldsymbol{x}} \cdot \dot{\boldsymbol{x}} = \boldsymbol{f} \cdot \boldsymbol{x},$$

or rather, on setting $w := m\dot{\boldsymbol{x}} \cdot \boldsymbol{x}$ **and** $2\,k := m\dot{\boldsymbol{x}} \cdot \dot{\boldsymbol{x}}$**,**

$$\boldsymbol{f} \cdot \boldsymbol{x} = \dot{w} - 2k.$$

Introduce the *time-average operator*

$$A[f] := \lim_{\tau \mapsto +\infty} \frac{1}{\tau} \int_0^\tau f(t)dt\,.$$

Then, for $f(t) = \dot{g}(t)$, we have that

$$A[f] = \lim_{\tau \mapsto +\infty} \frac{1}{\tau} \big(g(\tau) - g(0) \big) = 0,$$

provided that g only takes finite values; in particular,

$$A[\dot{w}] = 0.$$

An averaging of $\boldsymbol{f} \cdot \boldsymbol{x} = \dot{w} - 2k$ yields the *Virial Theorem*:

$$\boxed{A[\boldsymbol{f} \cdot \boldsymbol{x}] = -2\,A[k]}$$

Fluctuating forces

Langevin (1908) studies *Brownian particles suspended in a viscous fluid at rest* by means of macroscopic Newtonian mechanics:

$$m\ddot{\boldsymbol{x}} = \boldsymbol{f} + \boldsymbol{F},$$

where to standard Stokesian drag $\boldsymbol{f} = -\mu^{-1}\dot{\boldsymbol{x}}$ he

- **adds *fluctuating force $\boldsymbol{F}$*, giving the motion a *stochastic character*;**
- **makes use of lower alternative:**

$$\frac{1}{2}m\frac{d^2}{dt^2}(\boldsymbol{x}\cdot\boldsymbol{x}) + \frac{1}{2}\mu^{-1}\frac{d}{dt}(\boldsymbol{x}\cdot\boldsymbol{x}) = m\dot{\boldsymbol{x}}\cdot\dot{\boldsymbol{x}} + \boldsymbol{F}\cdot\boldsymbol{x};$$

- **takes *arithmetic mean* (no probabilistic expectation!) over large collection of identical particles;**
- ***characterizes the fluctuating force by assuming that the mean of the virial term $\boldsymbol{F}\cdot\boldsymbol{x}$ be null.***

Particle systems

- **Set**

$$\frac{d}{dt}\sum(m_i\dot{\boldsymbol{x}}_i\cdot\boldsymbol{x}_i)-\sum m_i\dot{\boldsymbol{x}}_i\cdot\dot{\boldsymbol{x}}_i=\sum\boldsymbol{f}_i\cdot\boldsymbol{x}_i\,,\quad \boldsymbol{f}_i=\sum_{j\neq i}\boldsymbol{f}_{ij}+\boldsymbol{f}_i^e$$

- **On choosing $o \equiv \boldsymbol{g}$ = *mass center*, get *Virial Theorem* in split form:**

$$\begin{cases} \boxed{A[\boldsymbol{F}\cdot\boldsymbol{g}]=-2\,A[K_{\boldsymbol{g}}]} \\ \boldsymbol{F}:=\sum\boldsymbol{f}_i^e,\;\; 2K_{\boldsymbol{g}}:=M\dot{\boldsymbol{g}}\cdot\dot{\boldsymbol{g}},\;\; M:=\sum m_i \\ \boxed{A\Big[\sum_{i>j}\sum(\boldsymbol{x}_i-\boldsymbol{x}_j)\cdot\boldsymbol{f}_{ij}+\sum\boldsymbol{x}_i\cdot\boldsymbol{f}_i^e\Big]=-2\,A[K_{rel}]} \\ 2K_{rel}:=\sum m_i\dot{\boldsymbol{x}}_i\cdot\dot{\boldsymbol{x}}_i \end{cases}$$

I.2 Deterministic Virial, Continuum and Eulerian

Eulerian balance of linear momentum

$$\boxed{\boldsymbol{0} = \boldsymbol{d}^{ni} + \textbf{div}\,\boldsymbol{T} - \rho\dot{\boldsymbol{v}},} \quad \boldsymbol{d}^{ni} = \textbf{dist. force}, \ \boldsymbol{T} = \textbf{Cauchy stress}$$

After dyadic multiplication by φ and integration by parts,

$$\boldsymbol{0} = \int_{P_t} \boldsymbol{\varphi} \otimes \boldsymbol{d}^{ni} + \int_{\partial P_t} \boldsymbol{\varphi} \otimes \boldsymbol{c} - \int_{P_t} (\textbf{grad}\,\boldsymbol{\varphi})\,\boldsymbol{T}^T - \int_{P_t} \rho\,\boldsymbol{\varphi} \otimes \dot{\boldsymbol{v}}, \ \ \boldsymbol{c} = \boldsymbol{T}\boldsymbol{n},$$

where $\boldsymbol{c}$ = contact forces at a point of ∂P_t. For $\boldsymbol{\varphi} \equiv \boldsymbol{x}$,

$$\int_{P_t} \rho\,\boldsymbol{x} \otimes \dot{\boldsymbol{v}} = \frac{d}{dt}\Big(\int_{P_t} \rho\,\boldsymbol{x} \otimes \dot{\boldsymbol{x}}\Big) - \int_{P_t} \rho\,\boldsymbol{v} \otimes \boldsymbol{v}\,, \quad \boldsymbol{v} = \dot{\boldsymbol{x}},$$

so that

$$\int_{P_t} \boldsymbol{x} \otimes \boldsymbol{d}^{ni} + \int_{\partial P_t} \boldsymbol{x} \otimes \boldsymbol{c} - \int_{P_t} \boldsymbol{T}^T = \frac{d}{dt}\Big(\int_{P_t} \rho\,\boldsymbol{x} \otimes \dot{\boldsymbol{x}}\Big) - \int_{P_t} \rho\,\boldsymbol{v} \otimes \boldsymbol{v}.$$

Recall

$$\boldsymbol{f}\cdot\boldsymbol{x} = \dot{w} - 2k \quad \Rightarrow \quad \boxed{A[\boldsymbol{f}\cdot\boldsymbol{x}] = -2\,A[k]}$$

Now, by taking the trace of

$$\int_{P_t} \boldsymbol{x}\otimes\boldsymbol{d}^{ni} + \int_{\partial P_t} \boldsymbol{x}\otimes\boldsymbol{c} - \int_{P_t} \boldsymbol{T}^T = \frac{d}{dt}\Big(\int_{P_t} \rho\,\boldsymbol{x}\otimes\dot{\boldsymbol{x}}\Big) - \int_{P_t} \rho\,\boldsymbol{v}\otimes\boldsymbol{v}\,,$$

we get

$$\left.\begin{array}{c} \int_{P_t} \boldsymbol{x}\cdot\boldsymbol{d}^{ni} + \int_{\partial P_t} \boldsymbol{x}\cdot\boldsymbol{c} - \int_{P_t} \mathbf{tr}\,\boldsymbol{T} = \dot{W}(P_t) - 2K(P_t) \\[2ex] W(P_t) = \int_{P_t} \rho\boldsymbol{x}\cdot\dot{\boldsymbol{x}},\;\; K(P_t) := \frac{1}{2}\int_{P_t} \rho\,\boldsymbol{v}\otimes\boldsymbol{v} \end{array}\right\} \Rightarrow$$

$$\Rightarrow \quad \boxed{A\Big[\int_{P_t} \boldsymbol{x}\cdot\boldsymbol{d}^{ni} + \int_{\partial P_t} \boldsymbol{x}\cdot\boldsymbol{c} - \int_{P_t} \mathbf{tr}\,\boldsymbol{T}\Big] = -2\,A[K(P_t)],}$$

a statement of the *Virial Theorem* in Continuum Mechanics.

By taking the symmetric part of

$$\int_{P_t} \boldsymbol{x} \otimes \boldsymbol{d}^{ni} + \int_{\partial P_t} \boldsymbol{x} \otimes \boldsymbol{c} - \int_{P_t} \boldsymbol{T}^T = \frac{d}{dt}\Big(\int_{P_t} \rho\, \boldsymbol{x} \otimes \dot{\boldsymbol{x}} \Big) - \int_{P_t} \rho\, \boldsymbol{v} \otimes ,$$

we get

$$\textbf{sym}\Big(\int_{P_t} \boldsymbol{x} \otimes \boldsymbol{d}^{ni} + \int_{\partial P_t} \boldsymbol{x} \otimes \boldsymbol{c} \Big) - \int_{P_t} \textbf{sym}\, \boldsymbol{T}^{\sharp} = \frac{1}{2}\, \ddot{\boldsymbol{I}}(P_t),$$

where

$$\boldsymbol{I}(P_t) := \int_{P_t} \rho\, \boldsymbol{x} \otimes \boldsymbol{x} = \textbf{\textit{Euler inertia tensor}} \textbf{ of part } P_t,$$

$$\boldsymbol{T}^{\sharp} := -\rho\, \boldsymbol{v} \otimes \boldsymbol{v} + \boldsymbol{T} = \textbf{\textit{virial stress}}.$$

Some call $\boldsymbol{T}^{\sharp}$ the *Reynolds stress*, because of the form of momentum balance typical of fluid mechanics that O. Reynolds liked:

$$\partial_t(\rho \boldsymbol{v}) + \textbf{div}(\rho\, \boldsymbol{v} \otimes \boldsymbol{v} - \boldsymbol{T}) = \boldsymbol{d}^{ni},$$

where $\rho\, \boldsymbol{v} \otimes \boldsymbol{v}$ = *convective current* and $-\boldsymbol{T}$ = *diffusive current*.

Lecture II - Probabilistic Virial

II.1 Recap of Statistical Mechanics

- **The microcanonical ensemble**
- **Microcanonical and time averages**
- **How to construct an equilibrium thermodynamics**

II.2 The Equipartition Theorem

II.3 The Virial Theorem

- **The Virial Theorem and the gas law**

Main references:

- J.P. Sethna, *Entropy, Order Parameters, and Complexity*. Oxford Master Series in Physics, Oxford Press, 2006.

- K. Huang, *Statistical Mechanics*. 2nd Ed. J. Wiley, 1987.

II.1 Recap of Statistical Mechanics

The microcanonical ensemble

Consider classical Hamiltonian system

- N **identical particles of invariable mass** m
- **confined in a 3D box of volume** V **(finite *molecular volume*** V/N**)**
- $H(q,p) = K(p) + U(q), \quad K(p) = \frac{1}{2} m^{-1} |p|^2, \;\; f(q) = -\partial_q U(q).$

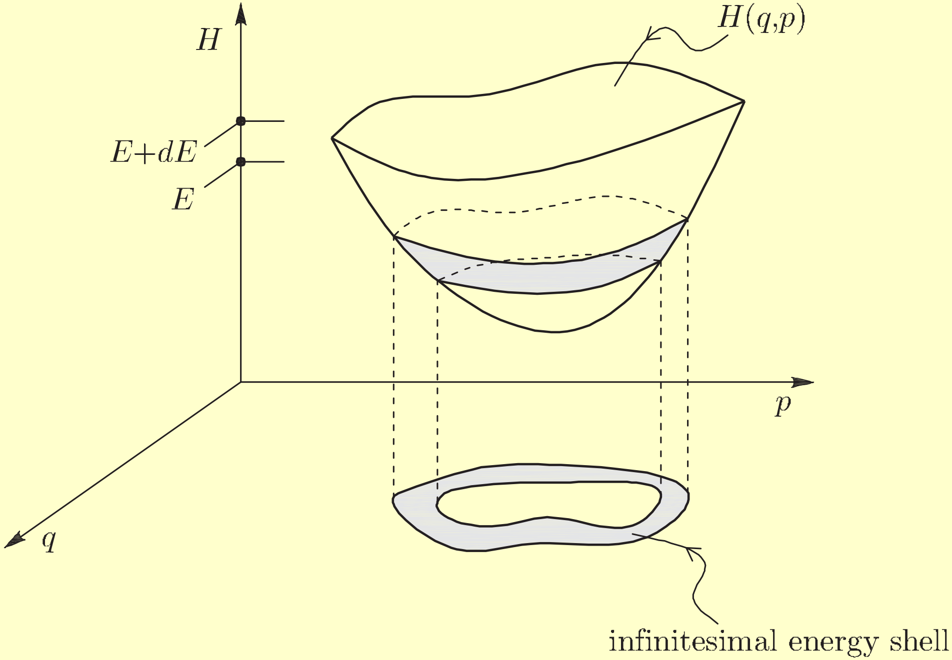
If both particle-particle and particle-wall collisions entail no energy losses, then *the total energy of the system is conserved*.

Three *macroscopic conservation conditions* – of number, volume, and energy – *define* the Gibbsian *microcanonical ensemble* $\{N, V, E\}$**.**

Note $\nexists$ **other motion-related conserved quantities: confinement in a box destroys both translational and rotational symmetries.**

- **for all practical purposes, *when a system is in equilibrium*, all microstates of the system having the same energy initially, and hence forever, are regarded as equivalent;**
- **all microstates accessed by the system along one of its trajectories have equal energy;**
- **(*ergodicity concept*) all ∞ly many microstates of a given energy are going to be visited, sooner or later, except perhaps a subset of measure zero .**

We now proceed *to measure* (not to count!) *'how many' initial states there are for a given assignment of initial energy*.



- $\Omega(E) = \int_{\mathcal{Z}} \theta(E - H(q,p))dqdp\,,\ \mathcal{Z} \equiv qp$**-plane**, $\theta(\cdot) =$ **Heaviside f.**

  = volume of subgraph of $H(q,p) = E$

- $\Omega(E + dE) - \Omega(E) = \int_{\mathcal{Z}} \big(\theta(E + dE - H(q,p)) - \theta(E - H(q,p))\big)dqdp$

  = volume of (infinitesimal) ***energy shell***

Heaviside vs. Dirac

Let D denote distributional differentiation. The distributional relationships between the Heaviside and Dirac functions is

$$-f(x_0) = \boxed{\int_{\mathbb{R}} \theta(x - x_0) f'(x)\, dx} = -\int_{\mathbb{R}} D\theta(x - x_0) f(x) dx$$

for all test functions f. Hence,

$$D\theta(x - x_0) = \delta(x - x_0).$$

- $\Omega'(E) = \int_{\mathcal{Z}} \delta(E - H(q,p))\, dqdp\,,\ \delta(\cdot) =$ **Dirac f.**
- ***volume partition f.*** **:=** $E \mapsto \Omega(E) = \int_{\mathcal{Z}} \theta(E - H(q,p))\, dqdp$
- ***surface partition f.*** **:=** $E \mapsto \omega(E) = \int_{\mathcal{Z}} \delta(E - H(q,p))\, dqdp$

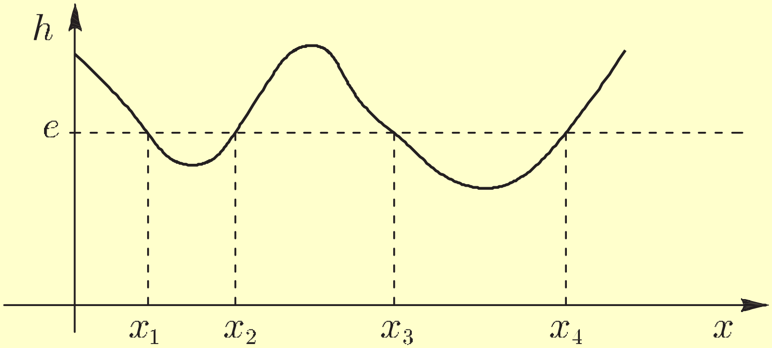
  measures boundary of region in $\mathcal{Z}$ **where** $H(q,p) \leq E$**.**

  Note that

$$\Omega'(E) = \omega(E)$$

- ***microcanonical probability meas.*****:=** $\tilde{\rho}_E(z) = \frac{1}{\omega(E)}\, \delta(E - H(z))$

Exercise



Let $h(x) \equiv 0$ **for** $x < 0$**,** $h(x) > e$ **for all** $x > x_4$**. Show that**

- $\Omega(e) = \int_{\mathbb{R}} \theta(e - h(x))\, dx = (x_2 - x_1) + (x_4 - x_3)$
- $\omega(e) = \int_{\mathbb{R}} \delta(e - h(x))\, dx = 1 + 1 + 1 + 1,$

  so that integration of $d\omega(e) = \delta(e - h(x))\, dx$ **literally counts all microstates** $x_1, \dots, x_4$ **where** $h(x) = e$**.**

Microcanonical and time averages

- ***microcanonical average*** **of** F**:**

$$\langle F\rangle(E) := \frac{1}{\omega(E)} \int_{\mathcal{Z}} F(q,p)\, \delta(E - H(q,p))\, dqdp$$

- (E,d)***-trajectory*****:**

  a trajectory of the N**-particle system under study, confined within a volume** V**, of energy** E **and duration** d

  $\Big[$ **that is, a solution** $t \mapsto (q(t), p(t)),\ \ t \in [0,d)$ **of the motion equations which complies with confinement condition and initial conditions** $(q(0), p(0))$**, and is such that** $H(q(0), p(0)) = E$**.** $\Big]$

- ***time average*** **of** F**:** $\overline{F}(E) := \lim_{d\to\infty} \frac{1}{d} \int_0^d F(q(t), p(t))dt.$

Microcanonical and time averages (cont.$^{\text{ed}}$)

Given a (E, d)-trajectory, one *assumes* that

- **(i)**

$$\langle F \rangle(E) \simeq \frac{1}{d} \int_0^d F(q(t), p(t))dt \,,$$

  with an approximation that becomes better and better the more accurately the given trajectory visits all parts of the state space where the energy takes the prescribed value;

- **(ii) when $d \to \infty$, the system tends to *statistical equilibrium*, that is, to a situation when *all quantities that are not conserved* (such as F itself) *are anyway independent of the initial conditions*.**

SM, MD, and the Ergodic Hypothesis

A basic assumption in SM – oftentimes referred to as the *ergodic hypothesis* – is that, for each given E,

$$\langle F\rangle(E) = \overline{F}(E), \quad \forall\, E,$$

so that *the microcanonical average can be calculated from a time average*.

The role of MD is precisely to allow for evaluating statistical averages via time averages along trajectories:

$$\underbrace{\text{statistical average at equilibrium}}_{SM} \simeq \underbrace{\text{time average along trajectories}}_{MD}$$

<u>Note</u> Averages and trajectories are to be chosen consistent with the ensemble that fits the system under study.

MD, CM, and experimental validation

Current MD simulations:

- **basic cell $\mathcal{X}$ of attomole size**
- **duration $\mathcal{T}$ of nanosecond order**

At the macroscopic scale of CM,

- **the space-time regions $\mathcal{X} \times \mathcal{T}$ considered by MD are to be regarded as (point, instant) pairs (x, t)**
- **the *measured value* $\widetilde{F}(x, t)$ of a field F should confirm the *prediction* $F(x, t)$ derived from solving an appropriate initial/boundary-value problem**

To relate $F(x,t)$ with $\overline{F}$ as evaluated by means of an MD simulation,

- **basic cell should be "large enough" (i.e., much larger than the correlation length of the spatial correlation function of interest)**
- **duration should be "long enough" (i.e., much longer than the relaxation time of the property of interest)**

Providing these quantitative conditions are met, MD furnishes a bridge between SM and CM:

$$\underbrace{\textbf{statistical average at equilibrium}}_{SM} \simeq \underbrace{\textbf{time average along trajectories}}_{MD}$$

$$\simeq \underbrace{\textbf{measured value}}_{CM} \; .$$

How to construct an equilibrium thermodynamics

(when working with the microcanonical ensemble in the background)

Step 1. Define an *entropy function*

$$S = \widehat{S}(E, V, N) = k_B \log Z(E) \qquad\qquad (*)$$

[***volume entropy* if** $Z(E) = \Omega(E)$**,** ***surface entropy* if** $Z(E) = \omega(E)$]

Step 2. For whatever entropy, solve for E the implicit equation $(*)$:

$$E = \widehat{U}(S, V, N) = \textit{internal-energy function}$$

Step 3. Define *temperature* $T := \partial_S E$

Step 4. Define the *Helmholtz free energy* to be the negative of the Legendre transform of the internal energy function:

$$\widehat{\Phi}(V, N, T) = E - T\widehat{S}(E, V, N), \quad T^{-1} = \partial_E S\,.$$

II.2 The Equipartition Theorem

Consider (microcanonical) expected value

$$\langle a_i \, \partial_{a_j} H \rangle (E) = \frac{1}{\omega(E)} \int_{\mathcal{Z}} a_i \, \partial_{a_j} H(z) \, \delta(E - H(z)) \, dz \, ,$$

where $a_i, a_j =$ ***microscopic degrees of freedom*** **of system whose Hamiltonian is** $H = \widehat{H}(q,p)$**.**

Generalized Equipartition Theorem

$$< a_i \, \partial_{a_j} H > (E) = (k_B T) \, \delta_{ij} \, , \quad T = \textit{equilibrium temperature}$$

Interpretation $< a_i \, \partial_{a_j} H >$ **measures '*conjugation wrt expectation*' of metavelocity** a_i **and metaforce** $\partial_{a_j} H$**;** ***GEP*** **is a statement of '*orthogonality wrt expectation*' of all (metavelocity, metaforce) pairs of different indices.**

Proof of *GEP*. 1/3

On recalling that

$$\delta(E - H(z)) = D\,\theta(E - H(z)),$$

the integral $\displaystyle\int_{\mathcal{Z}} a_i\,\partial_{a_j} H(z)\,\delta(E - H(z))\,dz$ **can be written as**

$$\int_{\mathcal{Z}} a_i\,\partial_{a_j} H(z)\,D\theta(E - H(z))\,dz = \partial_E\Big(\int_{\mathcal{Z}} a_i\,\partial_{a_j} H(z)\,\theta(E - H(z))\,dz\Big);$$

moreover,

$$a_i\,\partial_{a_j} H(z) = a_i \partial_{a_j}(H(z) - E) = \partial_{a_j}\big((H(z) - E)a_i\big) - (H(z) - E)\delta_{ij}.$$

Hence,

$$\omega(E) < a_i\,\partial_{a_j} H > (E) = -\partial_E\Big(\int_{\mathcal{Z}} \partial_{a_j}\big((E - H(z))a_i\big)\,\theta(E - H(z))\,dz\Big)$$
$$+\,\partial_E\Big(\int_{\mathcal{Z}} (E - H(z))\,\theta(E - H(z))\,dz\Big)\delta_{ij}\,.$$

Proof of *GEP*. 2/3

- **The integral** $\partial_E\Big(\int_{\mathcal{Z}} \partial_{a_j}\big((E-H(z))a_i\big)\,\theta(E-H(z))\,dz\Big)$ **vanishes, because**

$$\begin{aligned}\int_{\mathcal{Z}} \partial_{a_j}\big((E-H(z))a_i\big)\,\theta(E-H(z))\,dz &= \int_{\mathcal{R}} \partial_{a_j}\big((E-H(z))a_i\big)\,dz \\ &= \int_{\partial\mathcal{R}} (E-H(z))a_i\,(n_{\partial\mathcal{R}})_j\,da_{\partial\mathcal{R}} =\end{aligned}$$

for $\mathcal{R}$ **the region of** $\mathcal{Z}$ **where** $H(z) < E$ **and for** $\partial\mathcal{R}$ **its boundary, where** $H(z) = E$**.**

- $\int_{\mathcal{Z}} (E-H(z))\,\theta(E-H(z))\,dz = \int_{\mathcal{R}} (E-H(z))$, **whence**

$$\partial_E\Big(\int_{\mathcal{Z}} (E-H(z))\,\theta(E-H(z))\,dz\Big) = vol(\mathcal{R}) = \Omega(E).$$

Proof of *GEP*. 3/3

Thus,

$$\begin{aligned}\omega(E) < a_i\,\partial_{a_j} H > (E) &= -\partial_E \Big(\int_{\mathcal{Z}} \partial_{a_j} \big((E - H(z)) a_i \big)\, \theta(E - H(z))\, dz \Big) \\ &\quad + \partial_E \Big(\int_{\mathcal{Z}} (E - H(z))\, \theta(E - H(z))\, dz \Big) \delta_{ij} \\ &= \Omega(E) \delta_{ij}.\end{aligned}$$

At this point, with the sequential use of

- $\omega(E) = \Omega'(E)$
- $S = k_B \ln Z(E), \;\; Z(E) = \Omega(E); \quad \partial_E S = T^{-1}$

we deduce that

$$\begin{aligned}< a_i\,\partial_{a_j} H > (E) &= \frac{\Omega(E)}{\Omega'(E)}\, \delta_{ij} = \frac{1}{(\log \Omega(E))'}\, \delta_{ij} = \frac{k_B}{\partial_E \widehat{S}(E, V, N)}\, \delta_{ij} \\ &= k_B T \delta_{ij} \qquad \Box\end{aligned}$$

Equipartition of what? and among whom?

Consider an undamped *harmonic oscillator*: $H(q,p) = \frac{1}{2} m\,\omega^2 q^2 + \frac{1}{2} m^{-1} p^2$ **set** $H(q,p) = E$**; compute the *GEP* expression for each microscopic DOF:**

$$< q\,\partial_q H > (E) = k_B T = < p\,\partial_p H > (E)\,.$$

Then, the energy expectation is $< H > (E) = k_B T$, **and is split into equal parts** $\frac{1}{2} k_B T$ **for each microscopic DOF. More generally, the *GEP* yields:**

$$< q_i\,\partial_{q_i} H > (E) = k_B T = < p_i\,\partial_{p_i} H > (E) \quad (i\,(\textbf{unsummed}) = 1, 2, \ldots n)\,.$$

Whenever $\frac{1}{2} \sum_{i=1}^{n} \left(q_i\,\partial_{q_i} H + p_i\,\partial_{p_i} H \right) = H(q,p)$, **the total energy of the system is split into as many equal parts as the microscopic DOFs.**

II.3 The Virial Theorem

On recalling the motion equations,

$$< \sum_{i=1}^{n} q_i \, \partial_{q_i} H > (E) = - < \sum_{i=1}^{n} q_i \, \dot{p}_i > (E) = - < \sum_{i=1}^{n} q_i \, f_i(q) > (E) = n \, (k_B T)$$

The construct $\sum_{i=1}^{n} q_i \, f_i(q)$ **is called the *virial* of the system of forces acting on the system, in the configuration specified by** q**. At statistical equilibrium, the function** $E \mapsto < \sum_{i=1}^{n} q_i \, f_i(q) > (E)$ **delivers the ensemble average of the virial. The relation**

$$< \sum_{i=1}^{n} q_i \, f_i(q) > (E) = -n \, (k_B T)$$

is one expression of the *Virial Theorem*.

For another expression in the classical case when $p_i = m_i \dot{q}_i$, note that

$$\sum_{i=1}^{n} q_i \, f_i(q) = \dot{W}(q,p) - 2\,K(p)\,, \quad W(q,p) := \sum_{i=1}^{n} q_i p_i$$

Ergodicity allows to state the *Virial Theorem* as follows:

$$< \sum_{i=1}^{n} q_i \, f_i(q) > (E) = -2 < K(p) > (E),$$

whence

$$\boxed{< K(p) > (E) = n\Big(\frac{1}{2} k_B T\Big),}$$

an all important *relationship between the ensemble average of kinetic energy and temperature*.

The Virial Theorem and the gas law

The *ideal gas law*:

$$PV = \bar{n}RT, \quad \textbf{where } \bar{n} = n/n_A, \;\; n_A = \textbf{Avogadro's number},$$

as modified by van der Waals: $(P + \bar{n}^2\alpha V^{-2})(V - \bar{n}\beta) = \bar{n}RT$. **Now,**

$$\boxed{< \sum_{i=1}^{n} q_i \, f_i(q) > (E) = -n\,(k_B T)} \quad \Rightarrow \quad \textbf{right-hand side of gas law}.$$

As to the left-hand side, for V the volume of the container B and P the boundary pressure,

$$\begin{aligned} < \sum_{i=1}^{n} q_i \, f_i^{ext}(q) > (E) &\simeq \int_{\partial B} \boldsymbol{r} \cdot (-P\boldsymbol{n})\, da \\ &= -P \int_{\partial B} \boldsymbol{r} \cdot \boldsymbol{n}\, da = -3P\, vol(B) = -3\, PV. \end{aligned}$$

<u>Note</u> vdW corrections call for a less straightforward deduction from $< \sum_{i=1}^{n} q_i \, f_i^{int}(q) >$, the virial of internal forces.

Thank you for your kind attention!