Generalization of equipartition and virial theorems: Maximum Entropy derivation

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Outline

- Motivation: equipartition and virial theorems
- Continuous inference problem
- Theorem concerning Lagrange multipliers
- Examples: 1) equipartition and virial theorem

  2)temperature estimators: configurational temp.
- Conclusions

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Equipartition and virial theorems

K. Huang
Statistical Mechanics

6.4 EQUIPARTITION THEOREM

Let x_i be either p_i or q_i $(i = 1, \dots, 3N)$. We calculate the ensemble average of $x_i(\partial\mathscr{H}/\partial x_j)$, where $\mathscr{H}$ is the Hamiltonian. Using the abbreviation $dp\,dq \equiv d^{3N}p\,d^{3N}q$, we can write

$$\left\langle x_i \frac{\partial\mathscr{H}}{\partial x_j} \right\rangle = \frac{1}{\Gamma(E)} \int_{E<\mathscr{H}<E+\Delta} dp\,dq\,x_i \frac{\partial\mathscr{H}}{\partial x_j} = \frac{\Delta}{\Gamma(E)} \frac{\partial}{\partial E} \int_{\mathscr{H}<E} dp\,dq\,x_i \frac{\partial\mathscr{H}}{\partial x_j}$$

Noting that $\partial E/\partial x_j = 0$, we may calculate the last integral in the following manner:

$$\int_{\mathscr{H}<E} dp\,dq\,x_i \frac{\partial\mathscr{H}}{\partial x_j} = \int_{\mathscr{H}<E} dp\,dq\,x_i \frac{\partial}{\partial x_j}(\mathscr{H} - E)$$

$$= \int_{\mathscr{H}<E} dp\,dq \frac{\partial}{\partial x_j}[x_i(\mathscr{H} - E)] - \delta_{ij} \int_{\mathscr{H}<E} dp\,dq\,(\mathscr{H} - E)$$

The first integral on the right side vanishes because it reduces to a surface integral over the boundary of the region defined by $\mathscr{H} < E$, and on this boundary $\mathscr{H} - E = 0$. Substituting the latest result into the previous equation, and noting that $\Gamma(E) = \omega(E)\Delta$, we obtain

$$\left\langle x_i \frac{\partial\mathscr{H}}{\partial x_j} \right\rangle = \frac{\delta_{ij}}{\omega(E)} \frac{\partial}{\partial E} \int_{\mathscr{H}<E} dp\,dq\,(E - \mathscr{H})$$

$$= \frac{\delta_{ij}}{\omega(E)} \int_{\mathscr{H}<E} dp\,dq = \frac{\delta_{ij}}{\omega(E)} \Sigma(E)$$

$$= \delta_{ij} \frac{\Sigma(E)}{\partial\Sigma(E)/\partial E} = \delta_{ij} \left[\frac{\partial}{\partial E} \log \Sigma(E) \right]^{-1} = \delta_{ij} \frac{k}{\partial S/\partial E}$$

that is,

$$\left\langle x_i \frac{\partial\mathscr{H}}{\partial x_j} \right\rangle = \delta_{ij} kT \qquad (6.34)$$

This is the *generalized equipartition theorem*.

Inference with continuous variables

$\vec{x} = (x_1, \ldots, x_n)$ Distributed according to π(x)

New information: m expectation values $\langle f_i(\vec{x}) \rangle = F_i$

What is the new probability distribution $P(\vec{x})$?

Maximization of Shannon-Jaynes entropy:

$$S[P(\vec{x}), \pi(\vec{x})] = -\int d\vec{x} P(\vec{x}) \ln \frac{P(\vec{x})}{\pi(\vec{x})}$$

Result: $$P(\vec{x}) = \frac{1}{\mathcal{Z}(\vec{\lambda})} e^{-\vec{\lambda}\cdot\vec{f}(\vec{x})} \pi(\vec{x}),$$

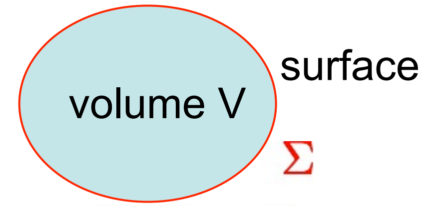
where $$\mathcal{Z}(\vec{\lambda}) = \int d\vec{x} \pi(\vec{x}) e^{-\vec{\lambda}\cdot\vec{f}(\vec{x})}$$

¿How can λ be obtained? → $$\vec{F} = -\frac{\partial}{\partial \vec{\lambda}} \ln \mathcal{Z}(\vec{\lambda}).$$

Estimators for λ

$$\left\langle A(\vec{x})\right\rangle_{\vec{\lambda},V} = \frac{1}{\mathcal{Z}}\int_V d\vec{x}\,\pi(\vec{x})e^{-\vec{\lambda}\cdot\vec{f}(\vec{x})}A(\vec{x}).$$

$u(\vec{x})$ $\qquad \nabla\cdot\vec{v}(\vec{x})$



$B(\vec{x}) = B_0$

$$\int_V d\vec{x}\,u\nabla\cdot\vec{v} = \int_\Sigma d\Sigma\,\hat{n}\cdot u\vec{v} - \int_V d\vec{x}\,\vec{v}\cdot\nabla u,$$

$$\hat{n} = \frac{\nabla B}{|\nabla B|}$$

$$\left\langle \nabla\cdot\vec{v}\right\rangle_{\vec{\lambda},V} = \frac{1}{\mathcal{Z}}\int_\Sigma d\Sigma\,\pi(\vec{x})e^{-\vec{\lambda}\cdot\vec{f}}\left(\frac{\vec{v}\cdot\nabla B}{|\nabla B|}\right) + \frac{1}{\mathcal{Z}}\int_V d\vec{x}\,e^{-\vec{\lambda}\cdot\vec{f}}\left[\pi(\vec{x})(\mathbb{J}^T\vec{\lambda})\cdot\vec{v} - \nabla\pi(\vec{x})\cdot\vec{v}\right]$$

"$\vec{\lambda}\nabla\cdot\vec{f}$"

$$\int d\vec{x}\,\pi(\vec{x})e^{-\vec{\lambda}\cdot\vec{f}}\delta(B_0 - B(\vec{x}))\vec{v}\cdot\nabla B.$$ and $$\delta(B_0 - B(\vec{x})) = \frac{\partial}{\partial B_0}\Theta(B_0 - B(\vec{x}))$$

we finally obtain

$$\left\langle \nabla\cdot\vec{v} - (\mathbb{J}^T\vec{\lambda})\cdot\vec{v} + \vec{v}\cdot\nabla\ln\pi(\vec{x})\right\rangle_{\vec{\lambda},V} = \frac{\partial}{\partial B_0}\left\langle \vec{v}\cdot\nabla B\right\rangle_{\vec{\lambda},V}$$

Conjugate variables theorem

$$\left\langle \nabla \cdot \vec{v} - (\mathbb{J}^T \vec{\lambda}) \cdot \vec{v} + \vec{v} \cdot \nabla \ln \pi(\vec{x}) \right\rangle_{\vec{\lambda},V} = \frac{\partial}{\partial B_0} \left\langle \vec{v} \cdot \nabla B \right\rangle_{\vec{\lambda},V}$$

Considering $V \longrightarrow \infty$

$$\left\langle \nabla \cdot \vec{v} \right\rangle_{\vec{\lambda}} = \left\langle (\mathbb{J}^T \vec{\lambda}) \cdot \vec{v} - \vec{v} \cdot \nabla \ln \pi(\vec{x}) \right\rangle_{\vec{\lambda}}.$$

“$\vec{\lambda} \nabla \cdot \vec{f}$”

SD, GG,
Phys. Rev. E, 051136 (2012)

System with only one constraint $\left\langle f(\vec{x}) \right\rangle = F_0$

$$\Longrightarrow \quad \lambda = \frac{\left\langle \nabla \cdot \vec{v} + \vec{v} \cdot \nabla \ln \pi \right\rangle_\lambda}{\left\langle \vec{v} \cdot \nabla f \right\rangle_\lambda}$$

Considering a flat prior $\nabla \ln \pi = 0$

$$\lambda = \frac{\left\langle \nabla \cdot \vec{v} \right\rangle_\lambda}{\left\langle \vec{v} \cdot \nabla f \right\rangle_\lambda}$$

Mechanical system: $\vec{x} = (p, q)$

Only one constraint $\langle \mathcal{H}(p,q) \rangle = E$

$$\Longrightarrow \quad P(\vec{x}) = \frac{1}{\mathcal{Z}(\vec{\beta})} e^{-\vec{\beta}\cdot\mathcal{H}(p,q)} \pi(p,q)$$

Conjugate variable theorem:

$$\beta = \frac{\left\langle \nabla \cdot \vec{v} \right\rangle}{\left\langle \vec{v} \cdot \nabla \mathcal{H} \right\rangle}$$

according to how the vector field $\vec{v}$ is chosen, we have several results, a family of temperature estimators

Equipartition and virial

$$\beta = \frac{\left\langle \nabla \cdot \vec{v} \right\rangle}{\left\langle \vec{v} \cdot \nabla \mathcal{H} \right\rangle}$$

1) choosing $\vec{v} = \hat{e}_k x_j$

$$\Longrightarrow \quad \beta = \frac{\delta_{kj}}{\left\langle x_j \frac{\partial \mathcal{H}}{\partial x_k} \right\rangle}$$

equipartition of energy:

$$x_j = p \Rightarrow k_B T = \frac{1}{2} m v^2$$

virial:

$$x_j = q \Rightarrow k_B T = -\vec{r} \cdot \vec{F}$$

Configurational temperature

$$\beta = \frac{\langle \nabla \cdot \vec{v} \rangle}{\langle \vec{v} \cdot \nabla \mathcal{H} \rangle}$$

Choosing $\vec{v} = \dfrac{\vec{\omega}}{\vec{\omega} \cdot \nabla \mathcal{H}}$

$$\Longrightarrow \quad \beta = \left\langle \nabla \cdot \frac{\vec{\omega}}{\vec{\omega} \cdot \nabla \mathcal{H}} \right\rangle$$

Taking $\vec{\omega} = \nabla \mathcal{H}$

$$\Longrightarrow \quad \beta = \left\langle \nabla \cdot \frac{\nabla \mathcal{H}}{|\nabla \mathcal{H}|^2} \right\rangle_E$$

(Dynamical temperature
H. H. Rugh,
Phys. Rev Lett (1998))

Conclusions

We have derived a general theorem that connects the values of Lagrange multipliers to expectation values of an arbitrary function

Application to physical systems allows one to obtain, in a practical way, different estimators to physical quantities (temperature, pressure, chemical potential, etc.)

There is a systematic method to evaluate the statistical efficiency of different estimators (like Cramer-Rao bound)