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Historical Papers

Violation of Boltzmann's H-Theorem in Real Gases
by E. T. Jaynes, 1971

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Review of Kinetic Theory

Hamiltonian Mechanics

$$\dot{p}_i = -\frac{\partial H}{\partial q_i} \quad , \qquad \dot{q}_i = \frac{\partial H}{\partial p_i}$$

$$\frac{df}{dt} = \frac{\partial f}{\partial t} + \sum_{i=1}^{6N} \frac{\partial f}{\partial q_i}\dot{q}_i + \frac{\partial f}{\partial p_i}\dot{p}_i$$

$$\frac{df}{dt} = \frac{\partial f}{\partial t} + \sum_{i=1}^{6N} \frac{\partial f}{\partial q_i}\frac{\partial H}{\partial p_i} - \frac{\partial f}{\partial p_i}\frac{\partial H}{\partial q_i}$$

$$\frac{df}{dt} = \frac{\partial f}{\partial t} + \{f, H\}$$

A Little Fluid Kinematics

- Incompressibility:

$$\partial_t \rho + v^i \partial_i \rho = 0$$

- Conservation of mass:

$$\partial_t \rho + \partial_i \left(\rho v^i\right) = 0$$

$$\partial_i v^i = 0$$

Liouville Equation

$$\partial_i v^i = \frac{\partial^2 H}{\partial q^i \partial p_i} - \frac{\partial^2 H}{\partial p_i \partial q^i} = 0$$

$$\frac{d}{dt} f = 0$$

$$\frac{\partial f}{\partial t} = \{H, f\}$$

Single-Particle Distribution

$$f_1(\vec{r},\vec{p}) := N\int\left(\prod_{i=2}^{N} d^3\vec{r}_i d^3\vec{p}_i\right) f(\{\vec{r}_i\},\{\vec{p}_i\})$$

$$\frac{\partial f_1}{\partial t} = N\int\left(\prod_{i=2}^{N} d^3\vec{r}_i d^3\vec{p}_i\right)\{H,f\}$$

$$H = \sum_{i=1}^{N}\frac{p_i^2}{2m} + V(\vec{r}_i) + \sum_{j<i} U(\vec{r}_i,\vec{r}_j)$$

1st BBGKY

$$H_1 = \frac{p^2}{2m} + V(\vec{r})$$

$$\frac{\partial f_1}{\partial t} = \{H_1, f_1\} + \left(\frac{\partial f_1}{\partial t}\right)_{coll.}$$

Boltzmann Equation

$$\left(\frac{\partial f_1}{\partial t}\right)_{coll.} = \int d^3\vec{p}_2 d^3\vec{p}_1' d^3\vec{p}_2' [\omega(\vec{p}_1', \vec{p}_2' | \vec{p}, \vec{p}_2) f_2(\vec{r}, \vec{r}, \vec{p}_1', \vec{p}_2') - \omega(\vec{p}, \vec{p}_2 | \vec{p}_1', \vec{p}_2') f_2(\vec{r}, \vec{r}, \vec{p}, \vec{p}_2)]$$

$$\left(\frac{\partial f_1}{\partial t}\right)_{coll.} = \int d^3\vec{p}_2 d^3\vec{p}_1' d^3\vec{p}_2' \omega(\vec{p}_1', \vec{p}_2' | \vec{p}, \vec{p}_2) [f_2(\vec{r}, \vec{r}, \vec{p}_1', \vec{p}_2') - f_2(\vec{r}, \vec{r}, \vec{p}, \vec{p}_2)]$$

Stosszahlansatz

$$f_2(\vec{r}, \vec{r}, \vec{p}, \vec{p}_2) = f_1(\vec{r}, \vec{p}) f_1(\vec{r}, \vec{p}_2)$$

H-Theorem

$$H(t) \coloneqq \int d^3\vec{r}\, d^3\vec{p}\, f_1(\vec{r},\vec{p}) \ln\big(f_1(\vec{r},\vec{p})\big)$$

$$\frac{dH}{dt} \leq 0$$

Violation of Boltzmann's H-Theorem in Real Gases

E. T. Jaynes, 1971 - Phys. Rev. A, Vol. 4, Num. 2

Violation of Boltzmann's H-Theorem in Real Gases

$$N = \int f(\vec{r}, \vec{v}, t)\, d^3\vec{r}\, d^3\vec{v}$$

$$K = \int \frac{1}{2} m v^2 f(\vec{r}, \vec{v}, t)\, d^3\vec{r}\, d^3\vec{v}$$

$$H = \int f \ln f \, d^3\vec{r}\, d^3\vec{v}$$

Violation of Boltzmann's H-Theorem in Real Gases

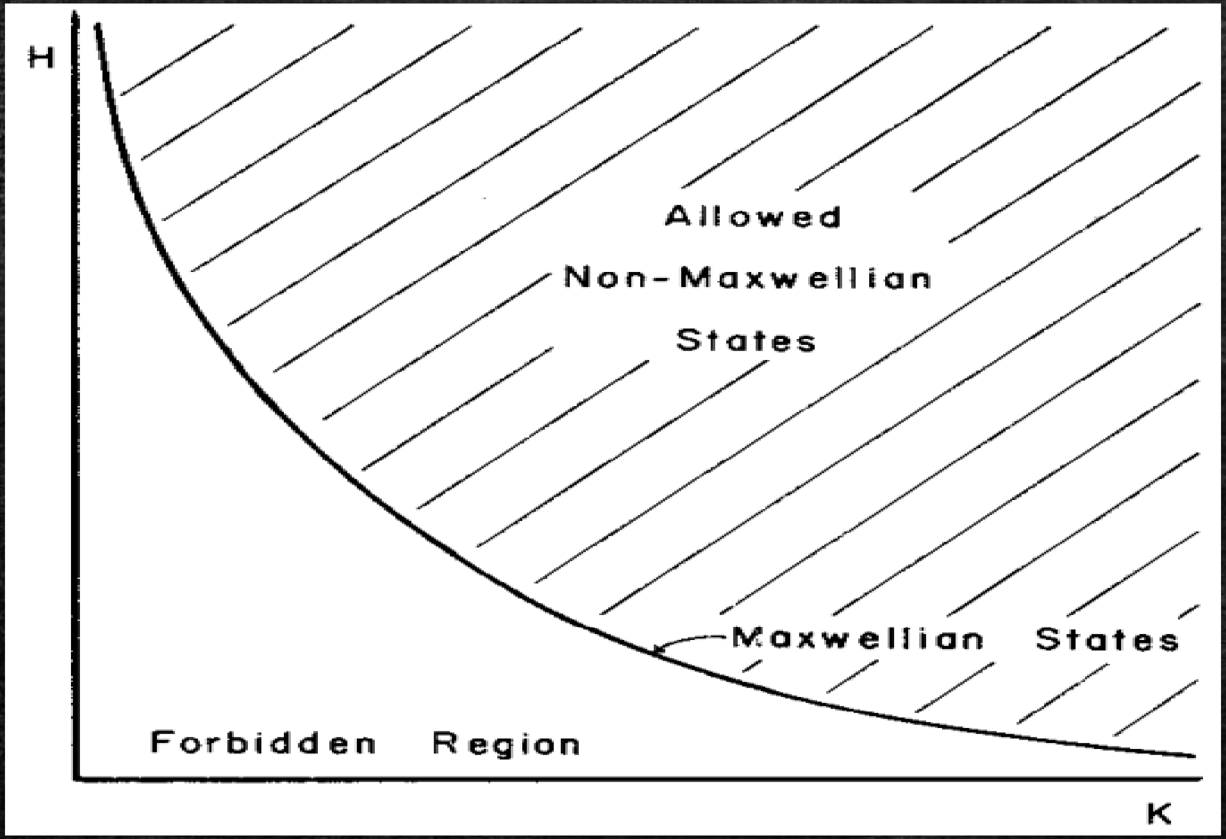
- Maxwellian Distributions:

$$f_M = \frac{N}{V}\left(\frac{\lambda}{\pi}\right)^{3/2} e^{-\lambda v^2}, \qquad \lambda = \frac{3Nm}{4K}$$

$$\ln z \leq z - 1$$

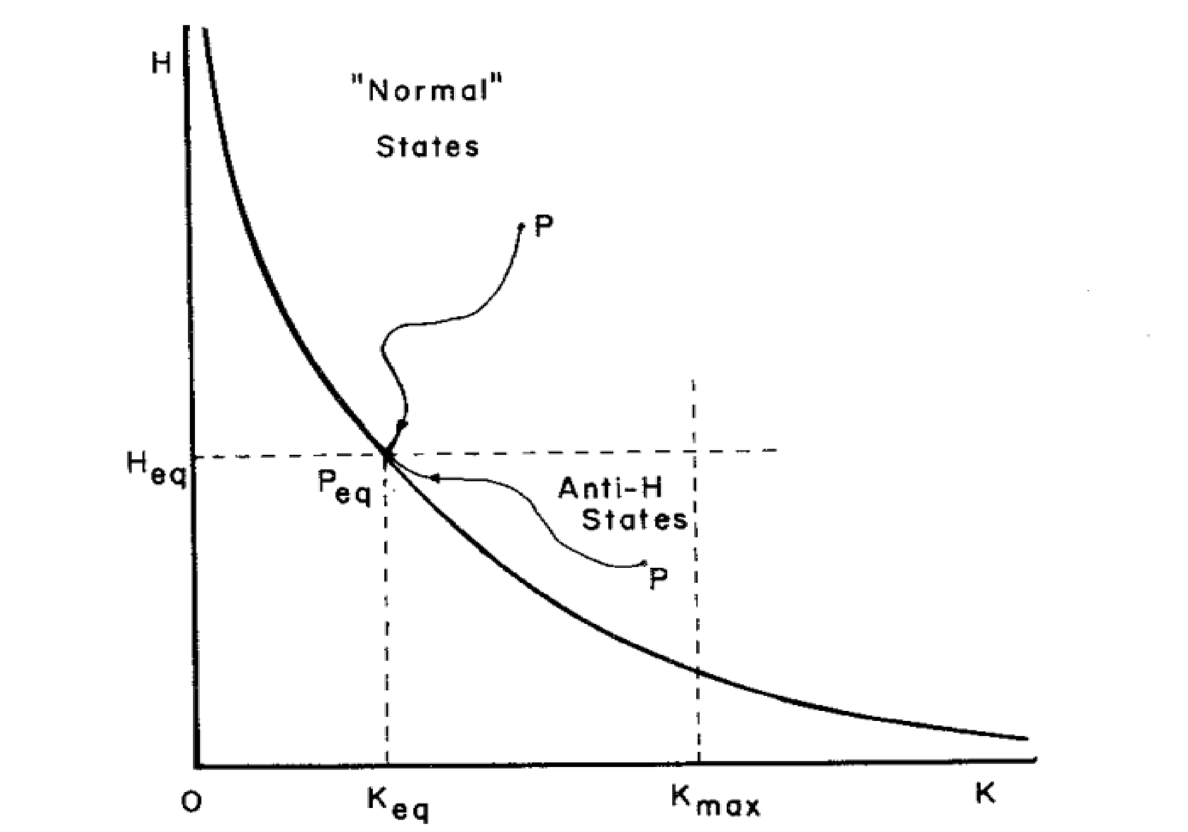
$$H \geq N\left[\ln\left(\frac{N}{V}\right) - \frac{3}{2} + \frac{3}{2}\ln\left(\frac{3Nm}{4\pi K}\right)\right]$$

Violation of Boltzmann's H-Theorem in Real Gases



Possible States in K-H Plane

Violation of Boltzmann's H-Theorem in Real Gases



Location of H-Theorem-Violating States

Violation of Boltzmann's H-Theorem in Real Gases

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Violation of Boltzmann's H-Theorem in Real Gases

$$H = C - N \ln V - \frac{3}{2} N \ln T$$

$$\left(\frac{\partial T}{\partial V}\right)_E < -\frac{2}{3}\frac{T}{V}$$

$$T\left(\frac{\partial P}{\partial T}\right)_V - P > \frac{2}{3} C_V \frac{T}{V}$$

Violation of Boltzmann's H-Theorem in Real Gases

$$\left(P + \frac{a}{V^2}\right)(V - b) = NkT$$

$$2C_V TV < 3a$$

$$\left(\frac{\partial h}{\partial T}\right)_V - \frac{PV}{T} > \frac{5}{3} C_V$$

Violation of Boltzmann's H-Theorem in Real Gases

- Mollier Chart: Oxygen

$$N = 1\, mol, \qquad T = 160°K, \qquad P = 45\, atm$$

$$\left(\frac{\partial h}{\partial T}\right)_V = 12\, cal/deg$$

$$\frac{PV}{T} = 1.3\, cal/deg$$

$$10.7 > 8.3$$

References & Sources

- [1]: D. Tong, Lectures on Kinetic Theory, University of Cambridge Graduate Course, 2012.
- [2]: R. Soto, Kinetic Theory and Transport Phenomena, Oxford University Press, 2016.
- [3] E. T. Jaynes, Violation of Boltzmann's H Theorem in Real Gases, Physical Review A, 4(2), 747–750 (1971).