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07. Kinetic Theory I

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Abstract
Part seven of course materials for Statistical Physics I: PHY525, taught by Gerhard Müller at the University of Rhode Island. Documents will be updated periodically as more entries become presentable.

Contents of this Document [ttc7]

7. Kinetic Theory I

Statistical uncertainty and information [tln37]

An experiment has n possible outcomes that occur with probabilities $P_1, P_2, \ldots, P_n$.

Properties that must be satisfied by any quantitative measure of *uncertainty*:

1. The uncertainty is a function of the probabilities of all possible outcomes: $\Sigma = \Sigma(P_1, P_2, \ldots, P_n)$.
2. The uncertainty is symmetric under all permutations of the P_i.
3. The maximum uncertainty occurs if all P_i are equal.
4. The uncertainty is zero if one of the outcomes has probability $P_i = 1$.
5. The combined outcome of two independent experiments has an uncertainty equal to the sum of the uncertainties of the outcomes of each experiment.

$$\Rightarrow \ \Sigma(P_1, P_2, \ldots, P_n) = -\sum_{i=1}^{n} P_i \ln P_i = -\langle \ln P \rangle.$$

Information comes in messages: $A_1, A_2, \ldots$. A message carries information only if it contains some news, i.e. something not completely expected.

$P(A)$: probability that message A is sent.
$I(A)$: information gain if message is indeed received.

The less likely the message, the greater the information gain if the message is received:

If $P(A) < P(B)$ then $I(A) > I(B)$, if $P(A) = 1$ then $I(A) = 0$.

If two independent messages are received, then the information gain is the sum of the information gains pertaining to each individual message:

$$P(A \cap B) = P(A)P(B) \ \Rightarrow \ I(A \cap B) = I(A) + I(B).$$

The information content of a message is equal to the change in (statistical) uncertainty at the receiver:

$$P_1, P_2, \ldots, P_n \xrightarrow{A} \bar{P}_1, \bar{P}_2, \ldots, \bar{P}_n \ \Rightarrow \ I(A) = \Sigma(P_1, P_2, \ldots, P_n) - \Sigma(\bar{P}_1, \bar{P}_2, \ldots, \bar{P}_n)$$

Information as used here refers only to the scarcity of events. Any aspects of usefulness and meaningfulness are disregarded.

[tex47] Statistical concept of uncertainty

An experiment has n possible outcomes that occur with probabilities $P_1, \ldots, P_n$. The uncertainty about the outcome of the experiment is defined as

$$\Sigma(P_1, \ldots, P_n) = -\sum_{i=1}^{n} P_i \ln P_i.$$

(a) Prove that the maximum uncertainty occurs if all P_i are equal.
(b) The n^2 combined outcomes of two independent experiments have probabilities $P_{ij} = P_i^I P_j^{II}$. Show that the uncertainty about the combined outcome of the two independent experiments is equal to the sum of the uncertainties of the outcomes of each experiment: $\Sigma(\{P_{ij}\}) = \Sigma(\{P_i^I\}) + \Sigma(\{P_i^{II}\})$.

Solution:

[tex48] Statistical uncertainty and information

The number of bird species living on some continent is known to be 100. An ornithologist visits a small island off the coast of that continent to find out how many of the 100 bird species have migrated to the island.
One month after her arrival on the island she sends a first message to the Ornithological Society, stating that there exist only five of the 100 bird species on the island.
A month later she sends a second message stating that the relative abundance of the five bird populations identified previously is 80%, 10%, 5%, 3%, 2%.
Determine the numerical value of the information contained in each message.

Solution:

[tex61] Information of sequenced messages

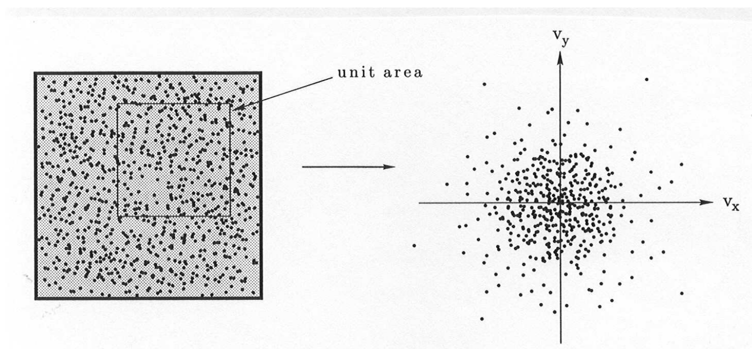
In which months of the year do Ellen, Nancy, and Susan have their birthdays? Three messages X, Y, Z about their birthdays are received by persons a, b, c:
Person a receives the messages in the sequence X, Y, Z.
Person b receives the messages in the sequence Z, X, Y.
Person c receives the messages in the sequence Y, Z, X.
The three messages are the following:
X: Nancy's birthday is in April.
Y: Ellen's birthday is in a later month than Nancy's birthday.
Z: Susan's birthday is in the same month as Ellen's birthday.
Find the numerical value of the information contained in the messages X, Y, Z as received by each person a, b, c.

Solution:

Kinetics of Classical Ideal Gas [tsl28]

- Gas consists of a large number of atoms.
- Motion of each atom is rectilinear with constant speed.
- Interactions are limited to collisions with walls or between atoms.
- Motion is randomized by collisions.
- Thermal equilibrium is characterized by uniform spatial distribution of atoms and by a velocity distribution $f(\mathbf{v})$ to be determined.

Position and velocity distribution in two dimensions.



Properties of velocity distribution $f(\mathbf{v})$:

- $\displaystyle\int d^3v f(\mathbf{v}) = 1 \quad \text{(normalization)},$
- $\displaystyle\int d^3v f(\mathbf{v})\,\mathbf{v} = 0 \quad \text{(symmetry)},$
- $\displaystyle\int d^3v f(\mathbf{v}) \left(\frac{1}{2}mv^2\right) = \frac{1}{2}m\langle v^2\rangle = \frac{U}{N} = \frac{3}{2}k_BT.$

Pressure [tex49]: $p = \dfrac{1}{3}\dfrac{N}{V}m\langle v^2\rangle = \dfrac{1}{3}\dfrac{N}{V}\,3k_BT \quad \Rightarrow \; pV = Nk_BT.$

[tex49] Pressure and mean square velocity in classical ideal gas

A classical ideal gas consisting of N atoms of mass m is confined to a container of volume V. The gas in thermal equilibrium with the walls is described by a spatially uniform distribution of atomic positions and an isotropic distribution of velocities $f(\mathbf{v})$. Show that the pressure exerted on the container walls is

$$p = \frac{1}{3}\frac{N}{V}m\langle v^2\rangle, \quad \text{where} \quad \langle v^2\rangle = \int d^3v\, v^2 f(\mathbf{v}).$$

Solution:

Maxwell velocity distribution [tln38]

Criteria used by Maxwell:

- statistical independence: $f(v_x, v_y, v_z) = f_1(v_x)f_1(v_y)f_1(v_z)$.
- spherical symmetry: $f_1(v_x)f_1(v_y)f_1(v_z) = f_1\left(\sqrt{v_x^2 + v_y^2 + v_z^2}\right) f_1(0)f_1(0)$.
- equipartition: $\frac{1}{2}m\langle v_\alpha^2\rangle = \frac{1}{2}k_BT, \quad \alpha = x, y, z.$

Velocity distribution:

$$\Rightarrow \; f(v_x, v_y, v_z) = \left(\frac{m}{2\pi k_BT}\right)^{3/2} \exp\left(-\frac{m(v_x^2 + v_y^2 + v_z^2)}{2k_BT}\right).$$

Speed distribution:

integrate $f(v_x, v_y, v_z)$ over shell $v < \sqrt{v_x^2 + v_y^2 + v_z^2} < v + dv$.

$$\Rightarrow \; f_s(v) = \frac{4}{\sqrt{\pi}}\left(\frac{m}{2k_BT}\right)^{3/2} v^2\, e^{-mv^2/2k_BT}.$$

Energy distribution:

Use $E = \frac{1}{2}mv^2, \quad v^2dv = \frac{1}{2}\left(\frac{2}{m}\right)^{3/2} E^{1/2}dE.$

$$\Rightarrow \; f_E(E) = \frac{2}{\sqrt{\pi}}(k_BT)^{-3/2}\sqrt{E}\, e^{-E/k_BT}.$$

Root-mean-square speed: $\sqrt{\langle v^2\rangle} = \sqrt{\frac{3k_BT}{m}}.$

Mean speed: $\langle v\rangle = \sqrt{\frac{8k_BT}{\pi m}}.$

Most frequent speed: $\left.\frac{df_s}{dv}\right|_{v_0} = 0 \;\Rightarrow\; v_0 = \sqrt{\frac{2k_BT}{m}}.$

[tex50] Maxwell velocity distribution (Maxwell's derivation)

In the original derivation of the velocity distribution $f(v_x, v_y, v_z)$ for a classical ideal gas, Maxwell used the following ingredients: (i) The Cartesian velocity components v_x, v_y, v_z (interpreted as stochastic variables) are statistically independent. (ii) The distribution $f(v_x, v_y, v_z)$ is spherical symmetric. (iii) The mean-square velocity is determined by the equipartition theorem. Determine $f(v_x, v_y, v_z)$ along these lines.

Solution:

[tex56] Maxwell distribution in D−dimensional space

The Maxwell velocity distribution of an ideal gas in D-dimensional space is

$$f(\mathbf{v}) = \left(\frac{m}{2\pi k_B T}\right)^{D/2} e^{-mv^2/2k_BT},$$

where $\mathbf{v} = (v_1, \ldots, v_D)$ and $v^2 = v_1^2 + \cdots + v_D^2$. Determine the associated speed distribution $f_S(v)$, the root-mean-square speed $\sqrt{\langle v^2 \rangle}$, the average speed $\langle v \rangle$, and the most frequent speed v_0 from $df_S/dv|_{v_0} = 0$.

Solution:

Boltzmann equation [tln39]

How does an arbitrary nonequilibrium velocity distribution $f(\vec{v}, t)$ approach equilibrium? Boltzmann's kinetic equation takes into account elastic pair collisions, characterized by a scattering cross section $\sigma(\vec{v}_1, \vec{v}_2; \vec{v}_1', \vec{v}_2')$ that depends on the velocities of the two particles before and after the collision.

During the infinitesimal time interval τ, the number of particles with velocities $\vec{v}_1 d^3v_1$ changes due to contributions A and B from two kinds of processes:

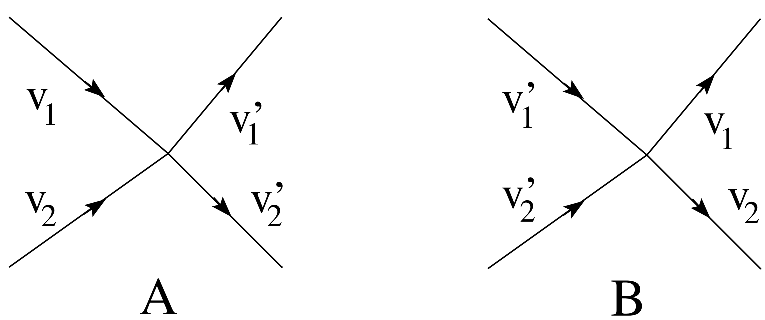
$$[f(\vec{v}_1, t+\tau) - f(\vec{v}_1, t)]\, d^3v_1 = B - A,$$

where the number of collisions away from $\vec{v}_1 d^3v_1$ is

$$A = \tau d^3v_1 \int d^3v_2 \int d^3v_1' \int d^3v_2'\, \sigma(\vec{v}_1, \vec{v}_2; \vec{v}_1', \vec{v}_2') f(\vec{v}_1, t) f(\vec{v}_2, t)$$

and the number of collisions into $\vec{v}_1 d^3v_1$ is

$$B = \tau d^3v_1 \int d^3v_2 \int d^3v_1' \int d^3v_2'\, \sigma(\vec{v}_1', \vec{v}_2'; \vec{v}_1, \vec{v}_2) f(\vec{v}_1', t) f(\vec{v}_2', t).$$



Here we have made the assumption of molecular chaos, which neglects correlations produced by the collisions: $f^{(2)}(\vec{v}_1, \vec{v}_2, t) = f(\vec{v}_1, t) f(\vec{v}_2, t)$.

Symmetry properties: $\sigma(\vec{v}_1, \vec{v}_2; \vec{v}_1', \vec{v}_2') = \sigma(\vec{v}_2, \vec{v}_1; \vec{v}_2', \vec{v}_1') = \sigma(\vec{v}_1', \vec{v}_2'; \vec{v}_1, \vec{v}_2)$.

Boltzmann equation for a spatially uniform velocity distribution:

$$\Rightarrow \frac{\partial}{\partial t} f(\vec{v}_1, t) = - \int d^3v_2 \int d^3v_1' \int d^3v_2'\, \sigma(\vec{v}_1, \vec{v}_2; \vec{v}_1', \vec{v}_2') \times \left[f(\vec{v}_1, t) f(\vec{v}_2, t) - f(\vec{v}_1', t) f(\vec{v}_2', t) \right].$$

Boltzmann's H-theorem [tln40]

Boltzmann's H-function: $H(t) \equiv \int d^3v_1\, f(\vec{v}_1,t) \ln f(\vec{v}_1,t)$.

$$\Rightarrow\ \frac{dH}{dt} = \int d^3v_1 \left[\frac{\partial f(\vec{v}_1,t)}{\partial t} \ln f(\vec{v}_1,t) + \frac{\partial f(\vec{v}_1,t)}{\partial t}\right].$$

Use $\int d^3v_1 \frac{\partial f(\vec{v}_1,t)}{\partial t} = \frac{d}{dt}\int d^3v_1\, f(\vec{v}_1,t) = 0$ and use Boltzmann equation.

$$\begin{aligned}\Rightarrow\ \frac{dH}{dt} = -& \int d^3v_1 \int d^3v_2 \int d^3v_1' \int d^3v_2'\, \sigma(\vec{v}_1,\vec{v}_2;\vec{v}_1',\vec{v}_2') \\ & \times \ln f(\vec{v}_1,t)\left[f(\vec{v}_1,t)f(\vec{v}_2,t) - f(\vec{v}_1',t)f(\vec{v}_2',t)\right].\end{aligned}$$

Likewise:

$$\begin{aligned} dH/dt &= \cdots\{\vec{v}_1 \leftrightarrow \vec{v}_2\},\ \{\vec{v}_1' \leftrightarrow \vec{v}_2'\}, \\ dH/dt &= \cdots\{\vec{v}_1 \leftrightarrow \vec{v}_1'\},\ \{\vec{v}_2 \leftrightarrow \vec{v}_2'\}, \\ dH/dt &= \cdots\{\vec{v}_1 \leftrightarrow \vec{v}_2'\},\ \{\vec{v}_2 \leftrightarrow \vec{v}_1'\}.\end{aligned}$$

$$\begin{aligned}\Rightarrow\ 4\frac{dH}{dt} = -& \int d^3v_1 \int d^3v_2 \int d^3v_1' \int d^3v_2'\, \sigma(\vec{v}_1,\vec{v}_2;\vec{v}_1',\vec{v}_2') \\ & \times \left[f(\vec{v}_1,t)f(\vec{v}_2,t) - f(\vec{v}_1',t)f(\vec{v}_2',t)\right] \\ & \times \left\{\ln\left[f(\vec{v}_1,t)f(\vec{v}_2,t)\right] - \ln\left[f(\vec{v}_1',t)f(\vec{v}_2',t)\right]\right\}.\end{aligned}$$

The function $h(x,y) \equiv (x-y)(\ln x - \ln y)$ is non-negative for $x,y > 0$ and is equal to zero if $x = y$.

Properties of $H(t)$: $\frac{dH}{dt} \leq 0$ and $\frac{dH}{dt} = 0$ if $f(\vec{v}_1,t)f(\vec{v}_2,t) = f(\vec{v}_1',t)f(\vec{v}_2',t)$.

The (stationary) velocity distribution which makes H stationary is the Maxwell distribution (Boltzmann's derivation).

Boltzmann's H-function is related to the uncertainty in our knowledge of the particle velocities as contained in the distribution $f(\vec{v}_1,t)$: $H(t) = -\Sigma_f$.

The stationary H-function is related to the entropy of an ideal gas at equilibrium: $S = -Nk_BH(\infty)$. Here the uncertainty in our knowledge of particle velocities is a maximum.

[tex57] Energy distribution for N ideal gas atoms.

The equilibrium velocity distribution for N atoms of a classical ideal gas is

$$f(\mathbf{v}_1, \ldots \mathbf{v}_N) = \left(\frac{m}{2\pi k_B T}\right)^{3N/2} e^{-m(v_1^2+\cdots+v_N^2)/2k_B T},$$

where $\mathbf{v}_i = (v_{ix}, v_{iy}, v_{iz})$.
(a) Determine the associated energy distribution $f_E(E)$, where $E = \frac{1}{2}m(v_1^2 + \cdots + v_N^2)$.
(b) Define the function $F_n(x)$ via $F_n(x)dx = f_E(E)dE$ with $x = E/nk_BT, n = 3N/2 - 1$ and plot $n^{-1}F_n(x),\ 0 < x < 4$ for $N = 1, 2, 10, 20$.
(c) How is the trend of this function for increasing N to be interpreted?

Solution:

[tex58] Maxwell's velocity distribution (Boltzmann's derivation)

The velocity distribution $f(\mathbf{v})$ is guaranteed to be a stationary solution of the Boltzmann equation if it satisfies the equation $f(\mathbf{v}_1)f(\mathbf{v}_2) = f(\mathbf{v}'_1)f(\mathbf{v}'_2)$, where $\mathbf{v}_1, \mathbf{v}_2$ and $\mathbf{v}'_1, \mathbf{v}'_2$ are the velocities before and after an elastic pair collison. Elasticity means that the four quantities $p_x = m(v_{1x} + v_{2x}), p_y = m(v_{1y} + v_{2y}), p_z = m(v_{1z} + v_{2z}), E = \frac{1}{2}m(v_1^2 + v_2^2)$ are conserved by the collision.
Boltzmann uses the following arguments: (i) The absence of any further conservation laws implies that $f(\mathbf{v}_1)f(\mathbf{v}_2) = F(p_x, p_y, p_z, E)$; (ii) in the relation $\ln f(\mathbf{v}_1) + \ln f(\mathbf{v}_2) = \ln F(p_x, p_y, p_z, E)$ the additivity of the two functions on the left-hand side implies that $\ln F$ is a linear function of its variables: $\ln F(p_x, p_y, p_z, E) = a_1 p_x + a_2 p_y + a_3 p_z + a_4 E + a_5$.
Show that if the five coefficients $a_1, \ldots, a_5$ are determined such as to satisfy the requirements $\int d^3v f(\mathbf{v}) = 1$ (normalization), $\langle \mathbf{v} \rangle = 0$ (symmetry), and $\frac{1}{2}m\langle v^2 \rangle = \frac{3}{2}k_BT$ (equipartition), then $f(\mathbf{v})$ is the Maxwell distribution.

Solution:

[tex59] Ideal−gas entropy and Boltzmann's H−function

Consider N particles of a classical monatomic ideal gas confined to a box of volume V at temperature T. Show that the entropy $S(T,V,N) = S_0 + nR\ln[(T/T_0)^{3/2}(V/V_0)]$ previously inferred from the empirical relations $pV = nRT, C_V = \frac{3}{2}nR$ can be derived via $S = -Nk_BH(\infty)$ from the stationary value of Boltzmann's H-function,

$$H(t) = \int d^3r \int d^3v\, f(\mathbf{r},\mathbf{v},t)\ln f(\mathbf{r},\mathbf{v},t).$$

Solution:

H-theorem and irreversibility [tln41]

Q: How does the preferred time direction, selected by the monotonic time-dependence of $H(t)$, follow from the underlying microscopic dynamics, which is invariant under time reversal?

A: The solution $f(\vec{v}_1, t)$ of the Boltzmann equation is to be interpreted as representing the properties of an ensemble of systems, i.e. the average behavior of systems that are prepared equally (on a macroscopic level).

Consider the function $\tilde{H}(t) = \displaystyle\int d^3v_1\, \tilde{f}(\vec{v}_1, t) \ln \tilde{f}(\vec{v}_1, t)$,

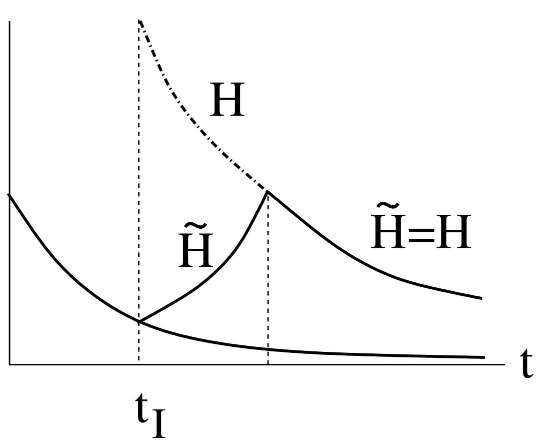
calculated via computer simulation, where $\tilde{f}(\vec{v}_1, t)$ now represents the velocity distribution of a single system.

Simulation data show that $\tilde{H}(t)$ tends to decrease and approach an asymptotic value just as the function $H(t)$ does.

Effect of velocity inversion at time t_I: $\tilde{H}(t)$ increases at $t > t_I$ for some time, then decreases again and approaches the same asymptotic value as $H(t)$ does.

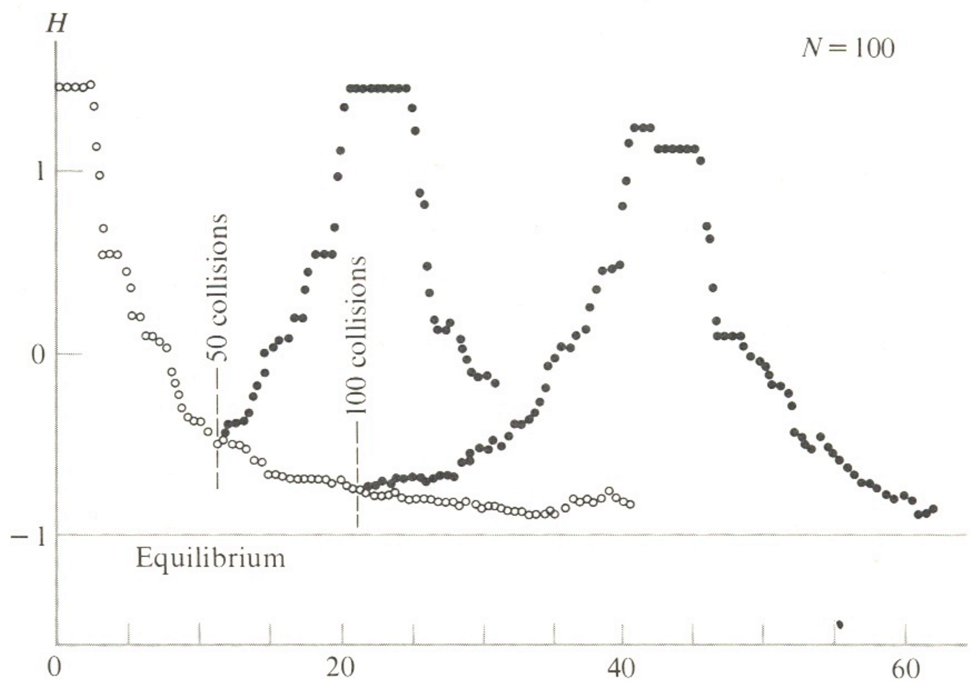
We can interpret $-\tilde{H}(t)$ as our uncertainty about the particle velocities in the system. The information contained in $\tilde{f}(\vec{v}_1, t)$ over and above the three general properties from which the Maxwell distibution was derived is $\tilde{H}(t) - \tilde{H}(\infty)$. However, this information is insufficient to carry out the velocity inversion.

Performing the velocity inversion requires an influx of information beyond what is contained in $\tilde{f}(\vec{v}_1, t)$, which causes a discontinuous drop in uncertainty of our knowledge about the particle velocities. At $t = t_I$, where the velocity inversion occurs, Boltzmann's function $H(t)$ jumps to a higher value and then decreases gradually as the information injected gets lost gradually in the wake of collisions.



Boltzmann's H-function simulated [tsl27]

Computer simulation of 100 hard disks moving in a 2D box and undergoing elastic collisions. Initial state: positions on a regular lattice, velocities random. Open circles: $H(t) = \int d^2v\, f(\mathbf{v}, t) \ln f(\mathbf{v}, t)$. Full circles: $H(t)$ when all velocities are inverted after 50 or 100 collisions.



[from Prigogine 1980]

[tex60] Maxwell distribution derived from minimizing the H−function

Minimize Boltzmann's H-function

$$H(t) = \int d^3v\, f(\mathbf{v},t) \ln f(\mathbf{v},t)$$

for the spacially uniform velocity distribution $f(\mathbf{v},t)$ of a classical ideal gas. Impose the integral constraints

$$\int d^3v\, f(\mathbf{v},t) = 1, \quad \frac{1}{2}m \int d^3v\, v^2 f(\mathbf{v},t) = \frac{3}{2}k_B T,$$

dictated by normalization and equipartition, respectively. Show that the resulting velocity distribution is Maxwellian.

Solution:

[tex63] Doppler broadening of atomic spectral lines

Consider a furnace containing a dilute gas at high temperature. Through a small window of the furnace, we observe a particular spectral line of the gas atoms by means of a spectrometer. The width of the observed spectral line is broadened due to the spread of velocities of the gas atoms. This effect is called *Doppler broadening*. The relativistic Doppler shift of the wavelength is $\lambda = \lambda_0\sqrt{(1+v/c)/(1-v/c)}$. For the case under consideration we can assume that $v/c \ll 1$. Show that the intensity profile is given by the expression

$$I(\lambda) \;\propto\; \exp\left(-\frac{mc^2(\lambda-\lambda_0)^2}{2\lambda_0^2 k_B T}\right),$$

where T is the temperature of the furnace, c is the speed of light, m is the mass of the gas atoms, and λ_0 is the wavelength of the radiation emitted by an atom at rest.

Solution: