2.3 Entropy [Gorbunov 5.2]

free energy $F = E - TS$

grand canonical potential

$$\Omega = F - \sum_\alpha \mu_\alpha Q_\alpha = E - TS - \sum_\alpha \mu_\alpha Q_\alpha$$

and $\Omega = -PV$ (Duhem - Gibbs)

$$S = \frac{1}{T}\left(E + PV - \sum_\alpha \mu_\alpha Q_\alpha\right)$$

densities : $s := \frac{S}{V}$, $n_\alpha := \frac{Q_\alpha}{V}$

$$s = \frac{1}{T}\left(\rho + P - \sum_\alpha \mu_\alpha n_\alpha\right)$$

$$d\Omega = -S\,dT - P\,dV - Q_\alpha\, d\mu_\alpha$$

$$\Omega = -PV$$

$$Q_\alpha = -\left(\frac{\partial \Omega}{\partial \mu_\alpha}\right)_{T,V} = V\left(\frac{\partial P}{\partial \mu_\alpha}\right)_T$$

ideal gas

$$P_i = \frac{1}{3}\int \frac{d^3p}{(2\pi)^3} f_i \frac{\vec{p}^{\,2}}{E_i}$$

contribution of particle species i to n_α :

expectation : $n_{\alpha i} = Q_{\alpha i}\, n_i$

check:

$$\frac{\partial P_i}{\partial \mu_\alpha} = \frac{1}{3}\int \frac{d^3p}{(2\pi)^3} \frac{\partial f_i}{\partial \mu_i} \underbrace{\frac{\partial \mu_i}{\partial \mu_\alpha}}_{=Q_{\alpha i}} \frac{\vec{p}^{\,2}}{E_i}$$

$$\frac{\partial}{\partial \mu} \frac{1}{e^{\beta(E-\mu)} \mp 1} = -\frac{\partial}{\partial E} \frac{1}{e^{\beta(E-\mu)} \mp 1}$$

$$\frac{\partial E}{\partial |\vec{p}|} = \frac{|\vec{p}|}{E} \quad , \qquad \frac{\partial}{\partial E} = \frac{E}{|\vec{p}|} \frac{\partial}{\partial |\vec{p}|}$$

$$\frac{\partial P_i}{\partial \mu_\alpha} = \frac{1}{3} Q_{\alpha i} \frac{4\pi}{(2\pi)^3} \underbrace{\int_0^\infty dp\, p^2 (-1) \frac{E_i}{p} \frac{\partial f_i}{\partial p} \frac{p^2}{E_i}}$$

$$\stackrel{!}{=} -\int_0^\infty dp \frac{\partial f_i}{\partial p} p^3 = 3 \int_0^\infty dp\, p^2 f_i$$

$$= Q_{\alpha i} \int \frac{d^3p}{(2\pi)^3} f_i = Q_{\alpha i} n_i \qquad \underline{\text{ok}}$$

For $m_i, \mu_i \ll T$: $\quad P_i = \frac{1}{3} \rho_i$,

$$s_i \simeq \frac{4}{3} \frac{\rho_i}{T} = \begin{cases} g_i \frac{2\pi^2}{45} T^3 \\ \frac{7}{8} g_i \frac{2\pi^2}{45} T^3 \end{cases}$$

s_i and number densities n_i differ by an order 1 factor.

non-relativistic

$$s_i = \frac{1}{T}\left(n_i m_i + \frac{3}{2} n_i T + n_i T - \sum_\alpha \mu_\alpha n_{\alpha i} \right)$$

$$= \frac{1}{T}\left(n_i m_i + \frac{5}{2} n_i T - \sum_\alpha \mu_\alpha Q_{\alpha i} n_i \right)$$

$$s_i = n_i \left(\frac{m_i - \mu_i}{T} + \frac{5}{2} \right)$$

We had

$$n_i = g_i \left(\frac{m_i T}{2\pi} \right)^{3/2} e^{(\mu_i - m_i)/T}$$

Use this to write s_i in terms of n_i only:

$$\frac{m_i - \mu_i}{T} = \ln \left(\frac{g_i}{n_i} \left[\frac{m_i T}{2\pi} \right]^{3/2} \right)$$

$$s_i = n_i \left\{ \frac{5}{2} + \ln \left(\frac{g_i}{n_i} \left[\frac{m_i T}{2\pi} \right]^{3/2} \right) \right\}$$

again, this typically of the order of n_i.
Furthermore, n_i of non-relativistic particles is usually much smaller than for relativistic ones.

example: $n_p \sim 10^{-10} n_\gamma$ for $T \ll 100\,\text{MeV}$

Consequence: entropy is dominated by relativistic particles

$$s \simeq g_* \frac{2\pi^2}{45} T^3$$

with the same g_* as for ρ.

entropy conservation

Second law of thermodynamics: the entropy of a closed system cannot decrease. It remains constant when the system remains in thermal equilibrium.

Then

$$dE = T\,dS - P\,dV + \sum_\alpha \mu_\alpha \, dQ_\alpha$$

Consider a comoving volume with $V = a^3$

Conservation of $Q_\alpha \Rightarrow dQ_\alpha = 0$

$$T\frac{dS}{dt} = T\frac{d(a^3 s)}{dt} = \frac{d(a^3\rho)}{dt} + P\frac{da^3}{dt} = \dot\rho + 3H(\rho + P)$$

GR: $\dot\rho + 3H(\rho+P) = 0$, follows from covariant conservation of $T^{\mu\nu}$, $T^{\mu\nu}{}_{;\mu} = 0$ $\Rightarrow$

$$\boxed{s a^3 = \text{const}}$$

This is used for quantitative description of conservation laws.

example: baryon number $n_B = \frac{B}{V}$ is often called <u>baryon asymmetry</u> because

$$B = \#\,\text{baryons} - \#\,\text{antibaryons}$$

(there are only particles with $B_i = \pm 1$)

$\frac{n_B}{s}$: t-independent characteristic of baryon asymmetry for $T \lesssim 1\,MeV$ $\eta = \frac{n_B}{n_\gamma}$ is constant

because photons are the only relativistic particles in equilibrium.