Basic principles of statistical physics

1. Definition of entropy: entropy is a logarithm of statistical weight:

$$S = \ln \Delta\Gamma, \quad \Delta\Gamma = \frac{\Delta p\, \Delta q}{(2\pi\hbar)^s}, \quad w(\bar{E})\, \Delta\Gamma = 1$$

$\Delta\Gamma$ - number of quantum states corresponding to the narrow maximum of distribution function w(E).

$$\int W(E)\, dE = 1, \qquad W(E) = \frac{d\Gamma(E)}{dE} w(E)$$

Entropy is a function of total energy E: S=S(E)

Temperature T in statistical physics is defined as inverse derivative dS/dE:

$$\frac{dS}{dE} = \frac{1}{T}$$

2. The law of increase of entropy, or the second law of thermodynamics

The sequence of states successively traversed by the system during its evolution corresponds to more and more probable distributions of energy. This increase in probability is in general very considerable, because the probability is given by e^S, where the entropy S of the system is an additive quantity. => The processes occurring in a non-equilibrium closed system go in such a way that the system continually passes from states of lower to those of higher entropy until finally the entropy reaches the maximum possible value, corresponding to complete statistical equilibrium.

Thus, if a closed system is at some instant in a non-equilibrium macroscopic state, the most probable consequence at later instants is a steady increase in the entropy of the system. This is the law of increase of entropy or second law of thermodynamics, discovered by R. Clausius (1865); its statistical explanation was given by L. Boltzmann in 1870s.

3. Gibbs distribution

Probability distribution of a quantum state with energy E_n is

$$w_n = A\exp\left(-\frac{E_n}{T}\right)$$

Derivation (our subsystem has energy E_n , environment has energy E', total system has energy E^0).

Probability w_n of each quantum state n of the subsystem is the statistical probability of environment to have energy E^0-E_n:

$$w_n = \text{const}\cdot\int \delta\left(E_n + E' - E^{(0)}\right) d\Gamma'$$

$$\frac{d\Gamma'}{dE'} = \frac{e^{S'(E')}}{\Delta E'} \Rightarrow w_n = \text{const}\cdot\left(\frac{e^{S'}}{\Delta E'}\right)_{E'=E^{(0)}-E_n}$$

$$S'\left(E^{(0)} - E_n\right) = S'\left(E^{(0)}\right) - E_n\frac{dS'\left(E^{(0)}\right)}{dE^{(0)}}, \quad \frac{dS}{dE} = \frac{1}{T}$$

4. The Maxwellian distribution

$$dw_v = \left(\frac{m}{2\pi T}\right)^{3/2} \exp\left[-\frac{m(v_x^2 + v_y^2 + v_z^2)}{2T}\right] dv_x\, dv_y\, dv_z$$

or $$dw_p = \frac{1}{(2\pi m T)^{3/2}} \exp\left(-\frac{p_x^2 + p_y^2 + p_z^2}{2mT}\right) dp_x\, dp_y\, dp_z$$

For one component $$dw_{v_x} = \sqrt{\frac{m}{2\pi T}}\, e^{-mv_x^2/2T}\, dv_x, \ldots$$

It is a classical analogue of the Gibbs distribution $$w_n = A \exp\left(-\frac{E_n}{T}\right)$$

$$dw = A \exp\left(-\frac{U(q)}{T} - \frac{K(p)}{T}\right) dp\, dq,$$

5. Free energy

Thermodynamic definition: $\overline{E} - TS = F$

Definition in statistical physics: $F = -T \ln \sum_n e^{-E_n/T}$

Partition function $Z = \sum_n e^{-E_n/T} = \mathrm{Sp}\,(e^{-\hat{H}/T})$

The Gibbs distribution $w_n = A \exp\left(-\frac{E_n}{T}\right) = \exp\left(\frac{F - E_n}{T}\right)$

derivation

Entropy $S = \ln \Delta\Gamma\,, \quad w(\overline{E})\,\Delta\Gamma = 1\,,$ ⇒

another definition $S = -\langle \ln w_n \rangle = -\ln A + \frac{\overline{E}}{T}\,,$

⇒ $\ln A = (\overline{E} - TS)/T = F/T$

6. Gibbs distribution for a variable number of particles

Distribution function (probability) of N particles and n-th quantum state

$$w_{nN}=\exp\left(\frac{\Omega+\mu N-E_{nN}}{T}\right)$$

This distribution is often called the grand canonical ensemble

Here Ω is the thermodynamic potential:

$$\Omega=-T\ln\sum_{N}\left[e^{\mu N/T}\sum_{n}e^{-E_{nN}/T}\right]$$

derivation

$$dS=\frac{dE}{T}+\frac{P}{T}dV-\frac{\mu}{T}dN$$

$$S'(E^{(0)}-E_{nN},\ N^{(0)}-N)\approx S'(E^{(0)},\ N^{(0)})-\frac{E_{nN}}{T}+\frac{\mu N}{T}$$

$$S=-\langle\ln w_{nN}\rangle=-\ln A-\frac{\mu\overline{N}}{T}+\frac{\overline{E}}{T}$$

7. Boltzmann distribution

The average numbers $n_k << 1$ of particles in the k-th quantum state, called the occupation numbers of k-th quantum state, are

$\bar{n}_k = \exp\left(\frac{\mu - \varepsilon_k}{T}\right)$, where μ is the chemical potential.

In classical statistics $n(p, q) = \exp\left(\frac{\mu - \varepsilon(p, q)}{T}\right)$

It gives the Maxwellian momentum distribution

$$dN_{\mathbf{p}} = \frac{N}{V(2\pi mT)^{3/2}} \exp\left[-\frac{p_x^2 + p_y^2 + p_z^2}{2mT}\right] dp_x\, dp_y\, dp_z,$$

and coordinate distribution $dN_{\mathbf{r}} = n_0 e^{-u(x, y, z)/T}\, dV$

Boltzmann's formula for the coordinate dependence of particle density $n(\mathbf{r}) = n_0 e^{-u(x, y, z)/T}$

8. Identical particles. Fermi distribution

The average numbers n_k of particles in the k-th quantum state, called the occupation numbers of k-th quantum state, are

$$\bar{n}_k = \frac{1}{e^{(\varepsilon_k - \mu)/T} + 1},$$ where μ is the chemical potential.

derivation

Pauli's principle: in each quantum state there cannot simultaneously be more than one particle.
The statistics based on this principle is called Fermi statistics, or Fermi-Dirac statistics.

Contribution to thermodynamic potential from the k-th state is

$$\Omega_k = -T \ln \sum_{n_k} \left(e^{\frac{\mu - \varepsilon_k}{T}}\right)^{n_k} = -T \ln\left(1 + e^{\frac{\mu - \varepsilon_k}{T}}\right)$$

The average numbers of particles in the k-th state

$$\bar{n}_k = -\frac{\partial \Omega_k}{\partial \mu} = \frac{e^{(\mu - \varepsilon_k)/T}}{1 + e^{(\mu - \varepsilon_k)/T}}$$

9. Identical particles. Bose distribution

The average numbers n_k of particles in the k-th quantum state, called the occupation numbers of k-th quantum state, are

$$\bar{n}_k = \frac{1}{e^{(\varepsilon_k - \mu)/T} - 1},$$ where μ is the chemical potential.

derivation

In each quantum state there can be any number of particles. The statistics based on this principle is called Bose statistics. It applies to all excitations and to groups of even number of fermions.

Contribution to thermodynamic potential from the k-th state is

$$\Omega_k = -T \ln \sum_{n_k=0}^{\infty} \left(e^{\frac{\mu - \varepsilon_k}{T}}\right)^{n_k} = T \ln\left(1 - e^{\frac{\mu - \varepsilon_k}{T}}\right)$$

The average numbers of particles in the k-th state

$$\bar{n}_k = -\frac{\partial \Omega_k}{\partial \mu} = \frac{1}{e^{(\varepsilon_k - \mu)/T} - 1}$$