Exam Statistical Mechanics
19 November 2018, 2-4pm

The total score is 20 points!

2 points

Diffusion

Consider N diffusing particles in one dimension and let D be the diffusion coefficient. Let us suppose that at time $t = 0$ the concentration is

$$c(x,0) = \frac{N}{\sqrt{2a^2\pi}}\, e^{-\dfrac{x^2}{2a^2}} \tag{1}$$

where a is given. Calculate $c(x,t)$ the concentration at later times.

3 points

Relativistic gas

Consider a system of N relativistic particles in a volume V and at a temperature T. In the limit of small masses the Hamiltonian is given by:

$$\mathcal{H} = c|\vec{p}|$$

a) Compute the canonical partition function for this system and derive the energy and specific heat. Show that the result is consistent with the equipartition theorem.

b) Determine the pressure as a function of volume, temperature and number of particles.

5 points

Two dimensional Harmonic Trap

A particle in two dimension is in equilibrium at temperature T and subject to the following potential

$$\phi(x,y) = \frac{k}{2}\left(x^2 + y^2\right) + \gamma xy$$

$(k, \gamma > 0)$ which keeps it bound close to the origin $x = y = 0$. For stability we also need to have $k > \gamma$, otherwise the potential is not bounded from below.

a) Calculate the average potential energy $\langle \phi \rangle$ from the analysis of the canonical partition function.

b) Calculate $\langle \phi \rangle$ using the equipartition theorem.

c) Calculate $\langle xy \rangle$.

5 points

Soft Spheres

In Soft Matter Physics some systems are described by "soft" potentials, which means that the particles can fully overlap. One example is polymers which are modeled as point particles interacting via the potential

$$\phi(r) = \varepsilon \exp\left(-\frac{r^2}{\sigma^2}\right)$$

with $\varepsilon > 0$.

a) Discuss the temperature behavior of the second virial coefficient $b_2(T)$ for this system. Is there a Boyle temperature?

b) Find explicitly the temperature dependence at high temperatures $k_B T \gg \varepsilon$.

5 points

Dieterici equation of State

The Dieterici equation of state is given by:

$$P(V - Nb) = N k_B T \, e^{-\frac{aN}{V k_B T}}.$$

where P, V and T are the pressure, volume and the number of particles. a and b are some positive parameters.

(a) Show that at sufficiently low densities or high temperatures this equation of state reduces to the ideal gas law.

At low densities a generic gas systems behaves as

$$P = n k_B T \left(1 + n b_2(T) + n^2 b_3(T) + n^3 b_4(T) + \ldots\right)$$

where $b_i(T)$ are the virial coefficients

(b) Calculate the second virial coefficient b_2 for the Dieterici equation of state and discuss the low and high temperature behavior. Does this behavior agree with your expectations?

(c) Calculate the Boyle temperature.

(d) Calculate the third virial coefficient and discuss its temperature dependence.

EXAM 19 NOVEMBER 2018

DIFFUSION

$$c(x,t) = \frac{N}{\sqrt{4\pi D(t+t_0)}} e^{-\frac{x^2}{4D(t+t_0)}}$$

IS SOLUTION OF THE DIFFUSION EQUATION

AT TIME $t=0$ $\quad c(x,0) = \frac{N}{\sqrt{4\pi D t_0}} e^{-\frac{x^2}{4Dt_0}}$

WE CHOOSE $t_0 = \frac{a^2}{2D}$ AND WE GET THE SOLUTION

$$c(x,t) = \frac{N}{\sqrt{4\pi Dt + 2a^2\pi}} e^{-\frac{x^2}{4Dt+2a^2}}$$

RELATIVISTIC GAS

$H = c|\vec{p}|$

a) $Z_1 = V\int d\vec{p}\, e^{-\beta c|\vec{p}|} = V\int_0^{+\infty} 4\pi p^2 e^{-\beta c p} dp = \frac{4\pi V}{(\beta c)^3} \underbrace{\overbrace{\int_0^{+\infty} x^2 e^{-x} dx}^{2}}_{\text{IRRELEVANT FOR THE REST OF THE PROBLEM}}$

TOTAL ENERGY $\quad E = -\frac{\partial}{\partial\beta}\log\frac{Z_1^N}{N!} = -N\frac{\partial}{\partial\beta}\log\beta^{-3}$

$$= 3Nk_BT$$

$C_V = \frac{\partial E}{\partial T} = 3Nk_B$

Equipartition $\quad \sum_{\alpha=\{x,y,z\}} \langle p_\alpha \frac{\partial H}{\partial p_\alpha}\rangle = 3k_BT$

$\frac{\partial H}{\partial p_\alpha} = c\frac{\partial}{\partial p_\alpha}\sqrt{p_x^2+p_y^2+p_z^2} = \frac{cp_\alpha}{|\vec{p}|}$ $\quad\Big\|\quad$ $\sum_\alpha \langle p_\alpha \frac{\partial H}{\partial p_\alpha}\rangle = \langle \frac{c|\vec{p}|^{\cancel{2}}}{\cancel{|\vec{p}|}}\rangle =$

$= \langle H\rangle = 3k_BT$ (ONE PARTICLE)

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THUS $\langle H \rangle = 3 k_B T$

AND FOR N PARTICLES $E = 3 N k_B T$ (AS FROM THE CALCUL. OF THE PARTITION FUNCTION)

b) $$p = -\frac{\partial F}{\partial V} = -k_B T \frac{\partial}{\partial V} \log \frac{Z_1^N}{N!}$$

$$= \frac{N k_B T}{V}$$ (AS IDEAL GAS, AS EXPECTED!)

TWO DIMENSIONAL HARMONIC TRAP

a) CONFIGURATIONAL PARTITION FUNCTION

$$Q = \int dx\,dy\; e^{-\beta\left[\frac{k}{2}(x^2+y^2) + \gamma x y\right]}$$

CHANGE OF VARIABLES $x' \equiv \sqrt{\beta}\, x \quad y' \equiv \sqrt{\beta}\, y$

$$Q = \frac{1}{\beta} \underbrace{\int dx'dy'\; e^{-\left[\frac{k}{2}(x'^2+y'^2) + \gamma x'y'\right]}}_{\text{INDEPENDENT ON } \beta}$$

$$E = -\frac{\partial \log Q}{\partial \beta} = \frac{1}{\beta} = k_B T$$

b)

EQUIPARTITION $$\left\langle x \frac{\partial \Phi}{\partial x} \right\rangle = k \langle x^2 \rangle + \gamma \langle xy \rangle = k_B T$$

$$\left\langle y \frac{\partial \Phi}{\partial y} \right\rangle = k \langle y^2 \rangle + \gamma \langle xy \rangle = k_B T$$

AS EXPECTED (SYMMETRY!) $\langle x^2 \rangle = \langle y^2 \rangle$

$$k_B T = k\langle x^2 \rangle + \gamma \langle xy \rangle = \frac{k}{2}\left(\langle x^2 \rangle + \langle y^2 \rangle\right) + \gamma \langle xy \rangle = \langle \Phi \rangle$$

WE ALSO HAVE FROM EQUIPARTITION

$$0 = \langle x \frac{\partial H}{\partial y} \rangle = k \langle xy \rangle + \gamma \langle x^2 \rangle$$

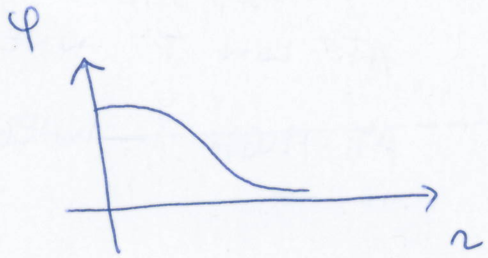
WE SOLVE
$$\begin{cases} k\langle x^2 \rangle + \gamma \langle xy \rangle = k_B T \\ \gamma \langle x^2 \rangle + k \langle xy \rangle = 0 \end{cases} \Longrightarrow \langle x^2 \rangle = -\frac{k}{\gamma} \langle xy \rangle$$

$$-\frac{k^2}{\gamma} \langle xy \rangle + \gamma \langle xy \rangle = k_B T \Longrightarrow \boxed{\langle xy \rangle = -\frac{\gamma k_B T}{k^2 - \gamma^2}}$$

NOTE $\langle xy \rangle < 0$

SOFT SPHERES

a) $\varphi(r) = \varepsilon e^{-r^2/\sigma^2}$



$$b_2(T) = -\frac{1}{2} \int d\vec{r} \left(e^{-\beta \varphi} - 1 \right)$$

AS $\varphi > 0$ $\quad b_2(T) > 0$ FOR ALL TEMPERATURES (AS EXPECTED FOR REPULSIVE INTERACTIONS)

THERE IS NO BOYLE TEMPERATURE

MOREOVER $b_2(T)$ IS A DECREASING FUNCTION OF T

$$\frac{\partial b_2}{\partial T} = \frac{\partial \beta}{\partial T} \frac{\partial b_2}{\partial \beta} = -\frac{1}{k_B T^2} \left(\frac{1}{2} \int d\vec{r}\, e^{-\beta \varphi} \varphi \right) < 0$$

b) AT HIGH TEMPERATURES $\beta \varphi \ll 1$

$$b_2(T) \simeq +\frac{1}{2} \int d\vec{r}\, \beta \varphi(\vec{r}) = \frac{\varepsilon}{2 k_B T} \int d\vec{r}\, e^{-r^2/\sigma^2} = \boxed{\frac{\varepsilon \pi^{3/2} \sigma^3}{2 k_B T}}$$

4) DIETERICI EQUATION OF STATE

$$P = \frac{n k_B T}{1 - nb} e^{-\frac{an}{k_B T}} \simeq n k_B T \left[1 + nb + n^2 b^2 \ldots\right]\left[1 - \frac{an}{k_B T} + \frac{1}{2}\frac{a^2}{(k_B T)^2} n^2 + \ldots\right]$$

$$= n k_B T \left[1 + n\left(b - \frac{a}{k_B T}\right) + n^2\left(b^2 - \frac{ab}{k_B T} + \frac{a^2}{2k_B^2 T^2}\right) + \ldots\right]$$

(a) FOR $n \to 0$ $\quad P \simeq n k_B T$ IDEAL GAS LAW

(b) $b_2(T) = b - \frac{a}{k_B T}$ AS THAT OF THE VAN DER WAALS MODEL

$b_2(T) < 0$ AT LOW T WHERE ATTRACTIONS DOMINATE

$b_2(T) > 0$ AT HIGH T WHERE REPULSIONS DOMINATE

(c) $k_B T_{BOYLE} = \frac{a}{b}$

(d) $b_3(T) = b^2 - \frac{ab}{k_B T} + \frac{a^2}{2k_B^2 T^2}$

$$= \frac{1}{2}\left[\left(\frac{a}{k_B T}\right)^2 - \frac{2ab}{k_B T} + b^2\right] + \frac{b^2}{2}$$

$$= \frac{1}{2}\left(b - \frac{a}{k_B T}\right)^2 + \frac{b^2}{2}$$ THIS IS ALWAYS POSITIVE