Freie Universität Berlin
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Statistical Physics and Thermodynamics (SS 2016)

Problem Sheet 12

Hand in:Thursday, July 14th during the lecture

http://www.physik.fu-berlin.de/en/einrichtungen/ag/ag-netz/lehre/

1. Kinetic & Potential Energies (4 points)

Consider a non-ideal system with particles interacting via power laws $\omega(q_1 - q_2) = |q_1 - q_2|^n$, where the Hamiltonian of such a system is expressed as: $\mathcal{H} = \mathcal{H}_{kin} + \mathcal{H}_{pot}$. The internal energy is therefore equal to $U = <\mathcal{H}> = k_B T \, \frac{3N}{n}(1 + \frac{n}{2}) - \frac{3}{n} V P$ as we derived in the lecture.

a) Calculate $< \mathcal{H}_{kin} >$ and $< \mathcal{H}_{pot} >$ for this system.

b) Show that for n=0 we retrieve the $< \mathcal{H}_{kin} >$, $< \mathcal{H}_{pot} >$ and U of an ideal gas.

c) Find $< \mathcal{H}_{kin} >$, $< \mathcal{H}_{pot} >$ and U for n=-1.

2. Third Virial Coefficient: Hard-Sphere Potential (8 points)

In the lecture we obtained the first and the second virial coefficients a_1 and a_2 for a non-ideal system with hard-sphere potential:

$$\omega(q_1 - q_2) = \begin{cases} \infty & |q_1 - q_2| < d \\ 0 & |q_1 - q_2| > d \end{cases} \tag{1}$$

Where a_l coefficients are obtained in terms of b_l coefficients using the following relations:

$$\frac{P}{k_B T} = \sum_l (\frac{z}{\lambda_t^3})^l b_l$$

$$\frac{P}{k_B T} = \sum_l a_l c^l$$

$$c = \sum_l l (\frac{z}{\lambda_t^3})^l b_l$$

Therefore we obtain:

$$a_1 = b_1 = 1$$

$$a_2 = -b_2 = -\frac{1}{2V} \int d^3 q_1 d^3 q_2 [F_{12}]$$

The third coefficient a_3 could be written as $a_3 = 4b_2^2 - 2b_3$ where $b_3 = \frac{1}{6V} \int d^3 q_1 d^3 q_2 d^3 q_3 [F_{12} F_{13} F_{23} + 3 F_{12} F_{23}]$ and $F_{ij} = e^{-\beta \omega(q_i - q_j)} - 1$.

Calculate the third virial coefficient a_3.

3. Virial Coefficients: Square Potential (8 points)

Consider a potential in the form:

$$\omega(r) = \begin{cases} \infty & 0 < r < \sigma \\ -E & \sigma < r < \sigma' \\ 0 & \sigma' < r < \infty \end{cases} \tag{2}$$

a) Calculate the first and the second virial coefficients a_1 and a_2 for this potential.

b) How does a_2 behave in the high temperature limit? Which term is dominant ?

C) How about low temperature? Explain which part of the potential is dominant.

d) Calculate the isothermal compressibility $\kappa_T = -\frac{1}{V}\frac{\partial V}{\partial P}\big|_{T,V}$ to the second order.

Step by Step Hints for Q2

1) Show that you can re-write the b_3 as the $b_3 = \frac{1}{6}\int d\vec{r}_{12} d\vec{r}_{13}[f(r_{12})f(r_{13})f(r_{23}) + 3f(r_{12})f(r_{23})]$. Where $f(r_{ij}) = F_{ij} = e^{-\beta\omega(r_{ij})} - 1$ and $\vec{r}_{ij} = \vec{q}_1 - \vec{q}_2$. Please note that $d\vec{r}_{ij}$ is in 3-dimensions.

2) The Fourier transform $\tilde{f}(k)$ is defined as $\tilde{f}(k) = \int d\vec{r} e^{i\vec{k}\vec{r}} f(r)$.The reverse Fourier transform is $f(r) = \int \frac{d\vec{k}}{(2\pi)^3} e^{-i\vec{k}\vec{r}} \tilde{f}(k)$

3) Write down the reverse Fourier transform of $f(r_{12})$, $f(r_{13})$ and $f(r_{23})$ and substitute them into the eq. for b_3. (Remember to use k, k' and k'' respectively)

4) Use the relation $\vec{r}_{23} = \vec{r}_{13} - \vec{r}_{12}$.

5) Use the definition of the Dirac delta function in three dimensions $\delta(\vec{r}) = \int \frac{d\vec{k}}{(2\pi)^3} e^{-i\vec{k}\vec{r}}$

6) Based on the definition of the delta function we have $\int d\vec{k} \tilde{f}(k)\delta(\vec{k} - \vec{a}) = \tilde{f}(a)$.

7) Show that you can write $\tilde{f}(k) = \int d\vec{r} e^{i\vec{k}\vec{r}} f(r) = \frac{4\pi}{k}\int_0^\infty dr\, r f(r)\sin(kr)$. (Just show a few first steps how you transform to dr $d\theta$ and $d\phi$, you do NOT need to show the integration steps)

8) Show that $\tilde{f}(-k) = \tilde{f}(k)^*$ and $\tilde{f}(k)^* = \tilde{f}(k)$. (Note that $\tilde{f}(k)^*$ is the complex conjugate of $\tilde{f}(k)$)

9) Use the following $\tilde{f}(k) = \frac{4\pi}{k}\int_0^a dr\, r f(r)\sin(kr) = 4\pi\frac{\sin(ak) - ak\cos(ak)}{k^3}$

10) Use $\int dk\, k^2[\frac{\sin(ak) - ak\cos(ak)}{k^3}]^3 = \frac{5}{96}a^6\pi$