Physics 504: Statistical Mechanics
Department of Physics, UIUC
Spring Semester 2013
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Problem Set No. 4:
Statistical Mechanics of Classical Interacting Gases
Due Date: March 16, 2013

1 The Mayer Linked Cluster Expansion

In the Lectures we discussed in detail the Mayer Linked Cluster Expansion for a classical gas with pair interaction with potential $U(\vec{r}_{ij})$, where $\vec{r}_{ij} = \vec{r}_i - \vec{r}_j$ is the relative separation of a pair of atoms (i, j). The gas is enclosed inside a very large container of volume V and the chemical potential is μ.

1. Use the Grand canonical Ensemble to determine a general expression for the pressure P in terms of the specific volume v, the temperature T and the chemical potential μ.

2. Give an explicit proof that only linked diagrams contribute to the expansion of the pressure P in a series expansion in powers of the fugacity z. Make sure that all the combinatorial coefficients work out.

3. Derive explicit expressions for the coefficients of the terms $O(z)$, $O(z^2)$, and $O(z^3)$ of the expansion of the presssure P. Write your results as integrals involving the pair-potential $U(\vec{r})$.

4. Show that, to this order in this expansion, the Grand Partition Function $\mathcal{Z}$ is an analytic function of the fugacity z, without zeros on the positive Real axis $z > 0$.

5. Show that, also to this order in the expansion, $P(z)$ is monotonically increasing function of z, and that $1/v(z)$ is monotonically increasing function of z.

6. Derive explicit formulas for the coefficients $a_0(T)$, $a_1(T)$ and $a_2(T)$, in the thermodynamic limit $V \to \infty$, of the virial expansion of the equation of state
$$\frac{Pv}{kT} = a_0(T) + a_1(T)\left(\frac{\lambda_T^3}{v}\right) + a_2(T)\left(\frac{\lambda_T^3}{v}\right)^2 + \dots$$
(where λ_T is the de Broglie thermal wavelength) in terms of integrals involving the pair interaction potential $U(\vec{r})$ and the temperature T.

7. Calculate the temperature dependence of the second virial coefficient $a_1(T)$ for a gas with the pair interaction

$$U(\vec{r}) = \begin{cases} \infty & \text{for } |\vec{r}| \leq a \\ -U_0 \left(\frac{r_0}{|\vec{r}|}\right)^6 & \text{for } |\vec{r}| > a \end{cases}$$

in the high temperature regime $kT \gg U_0$. Here a is the linear size of the hard core, r_0 is the range of the interaction while U_0 is the charcteristic energy scale of the pair interaction. Hint: expand the integrand in a power series expansion.

2 Statistical Mechanics of a Lattice Gas

In this problem you will consider a two-dimensional lattice gas on a square lattice like the one discussed in class in the context of the Lee-Yang Circle Theorem. In the case of a lattice gas there are no translational degrees of freedom and only the configurational degrees of freedom matter.

Let $\vec{r} = (n, m)a_0$ be the sites of a two-dimensional square lattice of lattice spacing a_0. Here n and m are integers, $n, m = 1, \ldots, M$ that label the sites of an $M \times M$ square lattice. We will consider a lattice of linear size $L = Ma_0$. The total number of sites is M^2 and the area is $A = L^2 = (Ma_0)^2$. The atoms of the lattice gas live on the sites of this lattice. Hence their coordinates are $\vec{r} = (n, m)a_0$, measured from the (arbitrary) origin of the lattice. We will be interested in the thermodynamic limit $A \to \infty$, *i. e.* $M \to \infty$, at fixed *density* of atoms, N/L^2, where N is the number of atoms. The atoms have a *hard core* interaction and an *attractive* interaction with strength $|U_0|$ only for atoms on nearest neighboring sites; otherwise there is no interaction. As usual we will denote the chemical potential by μ. The gas is at temperature T.

1. Develop a diagramatic method to organize the expansion of the Grand Partition Function $\mathcal{Z}$ in powers of the fugacity $z = \exp(\beta\mu)$. Make sure that your method counts all the contributions once and that all contributions are counted.

2. Use your diagramatic method to calculate the expansion of Grand Potential $\mathcal{F}$ as a function of the fugacity up to (and including) fourth order in the fugacity, z^4. Draw all the diagrams. Check that the Linked Cluster Theorem is obeyed.

3. Use your result to compute the coefficients of the virial expansion up to (and including) fourth order in powers of α/A, where α is a constant with units of area that you must determine. What determines α? Is it determined by a de Broglie wavelength? Why? Why not?