PHYS 301: Thermodynamics and Statistical Mechanics
Solutions to Problem Set #12

Question 1: Equation of State for a 2D Gas of Hard Discs

(a) Compute the Partition Function

The full partition function for N identical particles in 2D is given by:

$$Z(N, A, T) = \frac{1}{N!h^{2N}} \int \prod_{i=1}^{N} d^2p_i d^2x_i e^{-\beta H} \tag{1}$$

where the Hamiltonian is $H = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{i>j} U(r_{ij})$.

Since the exponential of a sum is the product of exponentials, we can separate the momentum integrals and the configuration (spatial) integrals:

$$Z = \frac{1}{N!h^{2N}} \left[\int \prod_{i=1}^{N} d^2p_i \exp\left(-\beta \frac{p_i^2}{2m}\right) \right] \left[\int \prod_{i=1}^{N} d^2x_i \prod_{i>j} e^{-\beta U(r_{ij})} \right] \tag{2}$$

The momentum integral separates into N identical 2D Gaussian integrals:

$$\int d^2p \exp\left(-\beta \frac{p^2}{2m}\right) = \int_0^\infty 2\pi p \exp\left(-\frac{\beta p^2}{2m}\right) dp = 2\pi m k_B T \tag{3}$$

Combining this with the $1/h^{2N}$ factor recovers the 2D thermal de Broglie wavelength, $\lambda_Q = \frac{h}{\sqrt{2\pi m k_B T}}$. The momentum part simply yields $(1/\lambda_Q^2)^N = 1/\lambda_Q^{2N}$.

For the configuration integral, we define the Mayer f-function as $f(r_{ij}) = e^{-\beta U(r_{ij})} - 1$, allowing us to rewrite the potential energy term:

$$\prod_{i>j} e^{-\beta U(r_{ij})} = \prod_{i>j} (1 + f(r_{ij})) \tag{4}$$

In the dilute limit ($A/N \gg r_0^2$), we expand this product and truncate it at the first-order pair interactions:

$$\prod_{i>j} (1 + f(r_{ij})) \approx 1 + \sum_{i>j} f(r_{ij}) \tag{5}$$

Integrating this over the $2N$ spatial coordinates:

$$\begin{aligned} \int d^{2N}x \left(1 + \sum_{i>j} f(r_{ij})\right) &= A^N + \frac{N(N-1)}{2} A^{N-1} \int d^2r f(r) \\ &\approx A^N \left(1 + \frac{N^2}{2A} \int d^2r f(r)\right) \end{aligned} \tag{6}$$

where we approximated the number of pairs $N(N-1)/2 \approx N^2/2$ for large N. Using the binomial approximation $(1+x)^N \approx 1+Nx$, we can write this sum as a power:

$$A^N \left(1+\frac{N^2}{2A}\int d^2r f(r)\right) \approx A^N \left(1+\frac{N}{2A}\int d^2r f(r)\right)^N \tag{7}$$

Thus, the partition function takes the desired form:

$$Z(N,A,T) = \frac{A^N}{N!\lambda_Q^{2N}}\left(1+\frac{N}{2A}\int d^2r f(r)\right)^N \tag{8}$$

Now, we compute the integral of the f-function. The hard-disc potential is $U(r)=\infty$ for $r<r_0$ and $U(r)=0$ for $r \geq r_0$. Therefore:

$$f(r) = \begin{cases} e^{-\infty}-1=-1 & \text{for } r<r_0 \\ e^0-1=0 & \text{for } r\geq r_0 \end{cases} \tag{9}$$

Evaluating the 2D spatial integral in polar coordinates:

$$\int d^2r f(r) = \int_0^{r_0} 2\pi r(-1)dr = -2\pi\left[\frac{r^2}{2}\right]_0^{r_0} = -\pi r_0^2 \tag{10}$$

Substituting this back gives the final partition function:

$$\boxed{Z(N,A,T) = \frac{A^N}{N!\lambda_Q^{2N}}\left(1-\frac{N\pi r_0^2}{2A}\right)^N} \tag{11}$$

(b) Compute the Helmholtz Free Energy

The Helmholtz free energy is $F=-k_BT\ln Z$. Using our result from part (a):

$$\begin{aligned} F &= -k_BT\ln\left[\frac{A^N}{N!\lambda_Q^{2N}}\left(1-\frac{N\pi r_0^2}{2A}\right)^N\right] \\ &= -k_BT\ln\left(\frac{A^N}{N!\lambda_Q^{2N}}\right) - Nk_BT\ln\left(1-\frac{N\pi r_0^2}{2A}\right) \end{aligned} \tag{12}$$

The first term is simply the free energy of a 2D ideal gas, F_{ideal}. For the second term, we are in the dilute limit ($A/N \gg r_0^2$), which means the second term inside the logarithm is very small. We can Taylor expand the logarithm using $\ln(1-x)\approx -x$:

$$\begin{aligned} F &\approx F_{\text{ideal}} - Nk_BT\left(-\frac{N\pi r_0^2}{2A}\right) \\ &= F_{\text{ideal}} + \frac{N^2\pi r_0^2 k_BT}{2A} \end{aligned} \tag{13}$$

$$\boxed{F(N,A,T) = -k_BT\ln\left(\frac{A^N}{N!\lambda_Q^{2N}}\right) + \frac{N^2\pi r_0^2 k_BT}{2A}} \tag{14}$$

(c) Compute the Equation of State

The pressure for this 2D system is given by the derivative of the free energy with respect to the area:

$$P = -\left(\frac{\partial F}{\partial A}\right)_{T,N} \tag{15}$$

Recall that $F_{\text{ideal}} = -Nk_BT \ln A +$ terms independent of A. Taking the derivative:

$$\begin{aligned} P &= -\frac{\partial}{\partial A}\left(F_{\text{ideal}} + \frac{N^2\pi r_0^2 k_BT}{2A}\right) \\ &= \frac{Nk_BT}{A} - \frac{N^2\pi r_0^2 k_BT}{2}\left(-\frac{1}{A^2}\right) \\ &= \frac{Nk_BT}{A} + \frac{N^2\pi r_0^2 k_BT}{2A^2} \end{aligned} \tag{16}$$

Factoring out the ideal gas term yields the equation of state:

$$\boxed{P = \frac{Nk_BT}{A}\left(1 + \frac{N\pi r_0^2}{2A}\right)} \tag{17}$$

Physical interpretation: This is the first-order correction to the ideal gas law. The positive correction term effectively increases the pressure due to the "excluded area" $\frac{1}{2}\pi r_0^2$ of the hard discs.