1. Suppose there is a vertical cylindrical container of cross section $s$ whose top wall is a movable piston of cross section $s$ with mass $M$. The piston is assumed to move only in the vertical direction ($z$-direction) and feels gravity. The container contains $N$ ($\gg 1$) classical noninteracting particles with mass $m$.

(1) Write down the Hamiltonian of the gas + piston system (write the piston vertical momentum as $p_M$).

(2) Obtain the pressure $P$ of the gas, and write the Hamiltonian in terms of $P$ and the volume of the gas $V = sz$, where $z$ is the position of the piston from the bottom of the container.

(3) Now, the mechanical variables are the phase variables of the gas system and the piston momentum $p_M$ and $V$. Compute the canonical partition function of the whole system.

(4) You should have realized that the calculation in (3), apart from the unimportant contribution in the thermodynamic limit of the piston momentum, is the calculation of the pressure ensemble. [That is, the heavy piston acts as a constant pressure device.] Obtain the equation of state of the gas in the cylinder (a trivial question).

2. Let us check the equivalence of grand canonical and canonical ensembles. That is, if we compute thermodynamic quantities in the thermodynamic limit, both give the same answers. Even experimentalists should look at this proof at least once in their lives.

The grand partition function $\Xi(T, \mu)$ and canonical partition function $Z(T, N)$ (the ground state energy is taken to be the origin of energy) are related as

$$\Xi(T, \mu) = \sum_{N=0}^{\infty} Z(T, N) e^{\beta \mu N}.$$ 

Let us assume that the system consists of $N$ (which is variable) particles in a box of volume $V$ and the total interaction potential $\Phi$ among particles is bounded from below by a number proportional to the number of particles $N$ in the system: $\Phi \geq -NB$, where $B$ is a (positive) constant. (The system Hamiltonian generally has the form of $H = K + \Phi$, where $K$ is the kinetic energy.)

Through answering the following almost trivial questions, we can demonstrate the ensemble equivalence (rigorously).

(1) Show that there is a constant $a$ such that

$$Z(T, N) \leq \left( a \frac{V}{N} \right)^N.$$  

Actually, show (classically)

$$Z(T, N) \leq Z_0(T, N) e^{\beta NB},$$

where $Z_0$ is the canonical partition function for the ideal gas (e.g., (1.7.3)). This is just eq. (1) above.
(2) Show that the infinite sum defining the grand partition function actually converges. The reader may use eq.(1) and $N! \sim (N/e)^N$ freely.

(3) Choose $N_0$ so that
\[ \sum_{N=N_0}^{\infty} Z(T,N)e^{\beta \mu N} < 1. \]

Show that this $N_0$ may be chosen to be proportional to $V$ (that is, $N_0$ is at most extensive).

(4) Show the following almost trivial bounds:
\[ \max_N Z(T,N)e^{\beta \mu N} \leq \Xi(T,\mu) \leq (N_0+1) \max_N Z(T,N)e^{\beta \mu N}. \]

(5) We are almost done, but to be explicit, show that $PV/Nk_BT$ obtained thermodynamically from the canonical partition function and that directly obtained from the grand partition function agree.

3. A single stranded DNA with a certain binding protein is stretched slowly until the protein dissociates from the DNA. Then, the length of the DNA is returned slowly to the rather relaxed original state where the binding of the molecule does not affect the DNA tension. The work $W$ dissipated during the cycle is measured at 300K and the experimental results were as follows:

<table>
<thead>
<tr>
<th>$W$ in pNnm</th>
<th>number of times</th>
</tr>
</thead>
<tbody>
<tr>
<td>78-82</td>
<td>4</td>
</tr>
<tr>
<td>83-87</td>
<td>15</td>
</tr>
<tr>
<td>88-92</td>
<td>7</td>
</tr>
<tr>
<td>93-97</td>
<td>4</td>
</tr>
<tr>
<td>98-102</td>
<td>1</td>
</tr>
</tbody>
</table>

What is the best estimate of the (Gibbs) free energy change due to binding of the protein in the relaxed state of the single stranded DNA? How is your estimate different from the simple average $\langle W \rangle$?

\[ ^1 \text{Inspired by Rustem Khafizov and Yan Chemla’s experiment on SSB. The numbers are only fictitious, although the magnitudes are realistic.} \]