CCP5 Summer School: Statistical Mechanics
Model solutions

1. Consider a system of N_A particles of type A and N_B particles of type B that lie on a lattice that contains $N = N_A + N_B$ total sites. Note that each of the A particles are indistinguishable from the other A particles, and the same holds for the B particles.

   Calculate the entropy of difference between a state where all the A and B particles are confined to different parts of the system and another state where both types can roam anywhere in the system. This is the entropy change of mixing. Use the Stirling approximation for $N!$ (i.e. $\ln N! \approx N \ln N - N$, when $N \gg 1$).

There is only one way to choose a configuration in which all the A particles are forced to lie in a specific part of the lattice and the B particles are force to lie on the remaining portion of the lattice. Therefore, $g = 1$ for this configuration, and, consequently $S = 0$.

In the situation where the A and B particles are allowed to be anywhere on the lattice, there are $N(N-1)\cdots(N-N_A+2)(N-N_A+1)$ ways to place the N_A particles on the lattice. However, these particles are indistinguishable, so the order in which we lay down the N_A particles is irrelevant. This means that $N_A!$ configurations are equivalent. So, in the end, there are only $N(N-1)\cdots(N-N_A+1)(N-N_A+2)/N_A!$ distinct ways to place the N_A particles on the lattice.

Once the A particles have been placed, the B particles need to be placed in the remaining $N - N_A$ lattice sites. There are $(N-N_A)(N-N_A-1)\cdots(2)(1)/N_B!$ ways of doing this, where the factor $N_B!$ accounts for the indistiguishability of the B particles.

Finally, we find that

$$g = \left[\frac{1}{N_A!} N(N-1)\cdots(N-N_A+2)(N-N_A+1)\right]$$
$$\times \left[\frac{1}{N_B!}(N-N_A)(N-N_A-1)\cdots(2)(1)\right]$$
$$= \frac{N!}{N_A!N_B!}$$
$$\ln g = \ln N! - \ln N_A! - \ln N_B!$$
$$\approx N \ln N - N - (N_A \ln N_A - N_A) - (N_B \ln N_B - N_B)$$
$$\approx (N_A + N_B)\ln N - (N_A + N_B) - (N_A \ln N_A - N_A) - (N_B \ln N_B - N_B)$$
$$\approx -N_A \ln \frac{N_A}{N} - N_B \ln \frac{N_B}{N}$$
$$\Delta S \approx -N_A k_B \ln x_A - N_B k_B \ln x_B$$

where $x_A = N_A/N$ is the mole fraction of A particles in the system, and $x_B = N_B/N$ is the mole fraction of B particles in the system. Note that this is the expression for the entropy of mixing for an ideal solution.

2. Consider a system of N free particles in which the energy of each particle can assume two and only two distinct values, 0 and ε ($\varepsilon > 0$). Denote by n_0 and n_1 the occupation numbers of the energy level 0 and ε, respectively. The total energy of the system is U.

(a) Find the energy for the system in terms of the occupation numbers.

(b) Find an expression for the entropy of the system in terms of the number of particles N and the total energy U.

(c) Find the temperature as a function of U, and show that it can be negative. Assume that the system is sufficiently large that the Stirling approximation (i.e. $\ln N! \approx N \ln N - N$) can be used.

(d) What happens when a system of negative temperature is allowed to exchange heat with a system of positive temperature?

This problem uses the microcanonical ensemble, where the total energy of the system and the number of particles are considered fixed.

(a) The energy of a particle in state 0 is 0, while the energy of a particle in state 1 is ε. The total energy of the system is just given by the sum of these two energies:
$$U = n_0(0) + n_1\varepsilon = n_1\varepsilon$$

(b) Given a value for the total energy U, the occupation of state 1 is $n_1 = U/\varepsilon$, and the occupation of state 0 is $n_0 - N - n_1$. In order to compute the entropy, we need to determine the total number of ways that the system can have a given occupation number n_1. This is just like trying to figure how probable a coin can land on heads n_1 times when it is flipped N times.

The total number Ω of microstates where the system has an energy U for N particles is:
$$\Omega(N, U) = \frac{N!}{n_0! n_1!} = \frac{N!}{(N - U/\varepsilon)!(U/\varepsilon)!}$$

The entropy is then
$$S(N, U) = k_B \ln \Omega(N, U)$$
$$S(N, U)/k_B = \ln N! - \ln(N - U/\varepsilon)! - \ln(U/\varepsilon)!.$$

(c) With the Stirling approximation, we find the entropy is given by
$$S(N, U)/k_B = N \ln N - N - n_0 \ln n_0 + n_0 - n_1 \ln n_1 + n_1$$
$$= N \ln N - n_0 \ln n_0 - n_1 \ln n_1$$
$$= N \ln N - (N - U/\varepsilon) \ln(N - U/\varepsilon) - (U/\varepsilon) \ln(U/\varepsilon),$$

where we have used the fact that $N = n_0 + n_1$.

The temperature is given by:
$$\frac{1}{T} = \left(\frac{\partial S}{\partial U} \right)_N$$
$$= \frac{k_B}{\varepsilon} \ln(N - U/\varepsilon) + \frac{k_B}{\varepsilon} - \frac{k_B}{\varepsilon} \ln(U/\varepsilon) - \frac{k_B}{\varepsilon}$$
$$= \frac{k_B}{\varepsilon} \ln \frac{N - U/\varepsilon}{U/\varepsilon}$$
$$= \frac{k_B}{\varepsilon} \ln \frac{1 - U/(N\varepsilon)}{U/(N\varepsilon)}$$

We note that the temperature is positive when $U < N\varepsilon/2$ and becomes negative when $U > N\varepsilon/2$. In otherwords, if $n_1/N < 1/2$ the system has a positive temperature, while if $n_1/N > 1/2$ the system has a negative temperature.

(d) Let us consider two systems that are placed together. One system has N' particles and energy $U' = n_1'\varepsilon$, while the other system has N'' particles and energy $U'' = n_1''\varepsilon$. Let's assume that $U' > N'\varepsilon/2$, so the first system has a negative temperature, and $U'' < N''\varepsilon/2$, so the second system has a positive temperature.

Now let us allow these two systems exchange energy with each other, keeping the total sum energy of both systems constant (i.e. $U = U' + U''$ is fixed). In other words, the composite system is adiabatic. When they are place in thermal contact, however, the occupation numbers of both systems may change. We will denote these new occupation numbers $\tilde{n}_1'$ and $\tilde{n}_1''$. These new occupation numbers will be the ones which maximize the entropy of the system, which is given by

$$\Omega = \frac{N'!}{\tilde{n}_1'!(N' - \tilde{n}_1')!} \frac{N''!}{\tilde{n}_1''!(N'' - \tilde{n}_1'')!}$$

$$\begin{aligned}
S/k_B &= \ln N'! - \ln \tilde{n}_1'! - \ln(N' - \tilde{n}_1')! + \ln N''! - \ln \tilde{n}_1''! - \ln(N'' - \tilde{n}_1'')! \\
&\approx N' \ln N' - N' - \tilde{n}_1' \ln \tilde{n}_1' + \tilde{n}_1' - (N' - \tilde{n}_1') \ln(N' - \tilde{n}_1') + (N' - \tilde{n}_1') \\
&\quad + N'' \ln N'' - N'' - \tilde{n}_1'' \ln \tilde{n}_1'' + \tilde{n}_1'' - (N'' - \tilde{n}_1'') \ln(N'' - \tilde{n}_1'') + (N'' - \tilde{n}_1'') \\
&\approx N' \ln N' - \tilde{n}_1' \ln \tilde{n}_1' - (N' - \tilde{n}_1') \ln(N' - \tilde{n}_1') \\
&\quad + N'' \ln N'' - \tilde{n}_1'' \ln \tilde{n}_1'' - (N'' - \tilde{n}_1'') \ln(N'' - \tilde{n}_1'') \\
&\approx N' \ln N' - \tilde{n}_1' \ln \tilde{n}_1' - (N' - \tilde{n}_1') \ln(N' - \tilde{n}_1') \\
&\quad + N'' \ln N'' - (n_1' + n_1'' - \tilde{n}_1') \ln(n_1' + n_1'' - \tilde{n}_1') \\
&\quad - (N'' - n_1' - n_1'' + \tilde{n}_1') \ln(N'' - n_1' - n_1'' + \tilde{n}_1')
\end{aligned}$$

where in the last relation, we used the fact that $n_1' + n_1'' = \tilde{n}_1' + \tilde{n}_1''$ due to the constraint in the total energy of the composite system.

To maximize this, we find the derivative of the entropy with respect to $\tilde{n}_1'$

$$\begin{aligned}
\frac{\partial S/k_B}{\partial \tilde{n}_1'} &\approx -\ln \tilde{n}_1' - 1 + \ln(N' - \tilde{n}_1') + 1 \\
&\quad + \ln(n_1' + n_1'' - \tilde{n}_1') + 1 - \ln(N'' - n_1' - n_1'' + \tilde{n}_1') - 1 \\
&\approx -\ln \tilde{n}_1' + \ln(N' - \tilde{n}_1') + \ln(n_1' + n_1'' - \tilde{n}_1') - \ln(N'' - n_1' - n_1'' + \tilde{n}_1') \\
&\approx \ln \frac{(N' - \tilde{n}_1')}{\tilde{n}_1'} - \ln \frac{(N'' - n_1' - n_1'' + \tilde{n}_1')}{(n_1' + n_1'' - \tilde{n}_1')}
\end{aligned}$$

If we set this to zero, then we see that equilibrium occurs when:

$$\ln \frac{(N' - \tilde{n}_1')}{\tilde{n}_1'} \approx \ln \frac{(N'' - n_1' - n_1'' + \tilde{n}_1')}{(n_1' + n_1'' - \tilde{n}_1')} = \ln \frac{(N'' - \tilde{n}_1'')}{\tilde{n}_1''}$$

This is just a restatement that the temperature of the two systems will be the same.

We can rearrange this relation to show that $\tilde{n}_1' < n_1'$, which implies that $\tilde{n}_1'' > n_1''$.

$$\frac{(N' - \tilde{n}_1')}{\tilde{n}_1'} \approx \frac{(N'' - \tilde{n}_1'')}{\tilde{n}_1''}$$

$$\frac{N'}{\tilde{n}_1'} \approx \frac{N''}{\tilde{n}_1''}$$

$$\frac{\tilde{n}_1'/n_1'}{\tilde{n}_1''/n_1''} \approx \frac{n_1''/N''}{n_1'/N'}$$

We assumed that the temperature of the first system was negative, which implies that $n_1'/N' > 1/2$, and that the temperature of the second system was positive, which implies that $n_1''/N'' < 1/2$. So the right side of the equation is less than one. Applying this value to the left side of the equation, we can deduce that $\tilde{n}_1' < n_1'$, indicating that energy moves from system with the negative temperature to the system with positive temperature!

3. Consider a classical system of N noninteracting diatomic molecules enclosed in a box of volume V at temperature T. The Hamiltonian for a *single* molecule is taken to be

$$H(\mathbf{p}_1, \mathbf{r}_1, \mathbf{p}_2, \mathbf{r}_2) = \frac{1}{2m}(p_1^2 + p_2^2) + \frac{k}{2}|\mathbf{r}_1 - \mathbf{r}_2|^2$$

where $\mathbf{p}_1$, $\mathbf{p}_2$, $\mathbf{r}_1$, and $\mathbf{r}_2$ are the momenta and positions of the two atoms in a molecule. Find

(a) the Helmholtz free energy of the system,

(b) the pressure of the system,

(c) the specific heat at constant volume, and

(d) the mean square molecular diameter $\langle|\mathbf{r}_1 - \mathbf{r}_2|^2\rangle$.

(a) For this problem we work in the canonical ensemble. The microstate of the system is

$$Q(N, V, \beta) = \int d\mathbf{p}_1^{(1)} d\mathbf{p}_2^{(1)} d\mathbf{r}_1^{(1)} d\mathbf{r}_2^{(1)} \cdots d\mathbf{p}_1^{(N)} d\mathbf{p}_2^{(N)} d\mathbf{r}_1^{(N)} d\mathbf{r}_2^{(N)}$$

$$\times\, e^{-\beta H(\mathbf{p}_1^{(1)}, \mathbf{p}_2^{(1)}, \mathbf{r}_1^{(1)}, \mathbf{r}_2^{(1)}) + \cdots - \beta H(\mathbf{p}_1^{(N)}, \mathbf{p}_2^{(N)}, \mathbf{r}_1^{(N)}, \mathbf{r}_2^{(N)})}$$

$$= \left[\int d\mathbf{p}_1 d\mathbf{p}_2 d\mathbf{r}_1 d\mathbf{r}_2\, e^{-\beta H(\mathbf{p}_1, \mathbf{p}_2, \mathbf{r}_1, \mathbf{r}_2)}\right]^N$$

$$= \left[\int d\mathbf{p}_1 d\mathbf{p}_2 d\mathbf{r}_1 d\mathbf{r}_2\, e^{-\frac{\beta}{2m}(p_1^2 + p_2^2) - \frac{\beta k}{2}|\mathbf{r}_1 - \mathbf{r}_2|^2}\right]^N$$

$$= \left[\int d\mathbf{p}_1 e^{-\frac{\beta p_1^2}{2m}} \int d\mathbf{p}_2 e^{-\frac{\beta p_2^2}{2m}} \int d\mathbf{r}_1 d\mathbf{r}_2\, e^{-\frac{\beta k}{2}|\mathbf{r}_1 - \mathbf{r}_2|^2}\right]^N$$

$$= \left[\int d\mathbf{p}_1 e^{-\frac{\beta p_1^2}{2m}} \int d\mathbf{p}_2 e^{-\frac{\beta p_2^2}{2m}} \int d\mathbf{R} \int d\mathbf{r}\, e^{-\frac{\beta k r^2}{2}}\right]^N$$

We can perform these integrals analytically, based on the following standard integral:

$$\int_{-\infty}^{\infty} dx\, e^{-x^2} = \pi^{1/2}$$

From a change of integration variable $x \to x/(\sqrt{2}\sigma)$, we find the relation:

$$\int_{-\infty}^{\infty} dx\, e^{-x^2/(2\sigma^2)} = (2\pi\sigma^2)^{1/2}.$$

This relation just give the normalization factor for a Gaussian distribution. Performing the required integrals, we find:

$$Q(N, V, \beta) = \left[\left(\frac{2\pi m}{\beta}\right)^{d/2}\left(\frac{2\pi m}{\beta}\right)^{d/2} V\left(\frac{2\pi}{\beta k}\right)^{d/2}\right]^N$$

$$\beta A = -N \ln\left(\frac{2\pi m}{\beta}\right)^d V\left(\frac{2\pi}{\beta k}\right)^{d/2}$$

where d is the dimensionality of the system.

(b) The pressure is simply given by

$$p = -\frac{\partial A}{\partial V}$$
$$= \frac{N}{\beta V}$$

This is just the ideal gas law.

(c) The energy E of the system is given by

$$E = \frac{\partial \beta A}{\partial \beta}$$
$$= \frac{d}{\beta} + \frac{d}{2\beta}$$
$$= \frac{3d}{2} k_B T$$

(d) The partition function for the bond length of a molecule is given by

$$q = \int d\mathbf{r}\, e^{-\beta k r^2/2}$$
$$= \left(\frac{2\pi}{\beta k}\right)^{d/2}$$

The average bond length for a single molecule is given by:

$$\langle r^2 \rangle = \frac{1}{q} \int d\mathbf{r}\, e^{-\beta k r^2/2} r^2$$
$$= -\frac{1}{q} \frac{\partial}{\partial \beta k/2} \int d\mathbf{r}\, e^{-\beta k r^2/2}$$
$$= -\frac{\partial}{\partial \beta k/2} \ln q$$
$$= -\frac{\partial}{\partial \beta k/2} \ln \left(\frac{2\pi}{\beta k}\right)^{d/2}$$
$$= \frac{d}{2} \frac{\partial}{\partial \beta k/2} \ln \frac{\beta k}{2\pi}$$
$$= \frac{d}{2} \frac{2}{\beta k}$$
$$= \frac{d k_B T}{k}$$