Statistical mechanics handout 4

Explain the difference between phase space and an ensemble.

Which extensive variables are fixed in the microcanonical ensemble.

Give a formula for the partition function

What is the probability of being in a particular microstate

Explain the connection between the microcanoncial partition function and a thermodynamic potential **Ensembles** As discussed in handout three the atoms in any physical system can adopt any one of a large number of micorstates. For a quantum system these microstates are the various quantum levels the system can be in, while for a classical system these microstates are the various combinations of positions and velocities the atoms can have. Regardlessly, we refer to the set of all these microstates as phase space. As discussed in the previous handout statistical mechanics is concerned with calculating the probability of being in any given microstate.

The microstates that any physical system can adopt will depend on the walls that are placed around it. If the system is surrounded by walls that are impermeable to heat, work and matter then the system will be confined to a set of microstates that all have the same energy, volume and temperature. If the system has walls that can exchange heat but that are impermeable to work and matter then the system will be confined to a set of microstates that all have the same volume and temperature. However, as long as they satisfy the constraints on the volume and number of atoms microstates with all possible energies are permissible. We call the set of states that are accessible to a system surrounded by walls the ensemble. Clearly, the set of microstates in any given ensemble is a subset of the set of microstates in phase space.

The microcanonical (NVE) ensemble In statistical mechanics when we develop models for isolated systems we use the microcanonical ensemble. Neither material, work nor heat can be exchanged with isolated systems so such systems have constant volume, constant number of atoms and constant internal energy. As such these system can only be in microstates that have energy, E, volume, V and number of atoms N. In other words none of the extensive thermodynamic variables need to be calculated by averaging and the only constraint when we perform our constrained optimisation is the requirement of normalisation. Consequently, if there are Ω microstates that have energy E, volume V and number of atoms N the microcanonical partition function is given by:

$$Z_{mc}(N, V, E) = \Omega$$

Furthermore, the probability of being in a particular microstate is simply:

$$p_i = \frac{1}{Z_{mc}(N, V, E)}$$

as long as the microstate in question has energy E, volume V and number of atoms N. The appropriate thermodynamic potential for this ensemble is the entropy, which can be calculated from the partition function using:

$$S(N, V, E) = k_B \ln Z_{mc}(N, V, E)$$

Summary

To make the connection between classical thermodynamics and the statistical behaviour of atoms we have to incorporate the effect of the walls surrounding the system. Walls fix the values of certain extensive variables and will thus force the system to be in one of the microstates in a subset of phase space (the ensemble). The microcanonical ensemble has fixed number of atoms, fixed volume and fixed internal energy.

Which extensive variables are fixed in the canonical ensemble

Give a formula for the canonical partition function

Give the probability for being in a particular microstate in the canonical ensemble

Which is the appropriate thermodynamic potential to use when considering the behaviour of the canonical ensemble

Describe two ways in which one can calculate the ensemble average of the energy

Explain how the heat capacity can be calculated The canonical (NVT) ensemble In statistical mechanics when we develop models for closed systems that cannot do PV work we use the canonical ensemble. Neither material nor work can be exchanged with closed systems that cannot do PV work so such system have constant volume and constant number atoms. The energy, however, has to be calculated as an ensemble average. Inserting these requirements into the expression for dS that we derived on worksheet 3 we arrive at:

$$\frac{\mathrm{d}S}{k_B} = -\lambda^{(1)} \left\langle \frac{\partial E}{\partial N} \right\rangle \mathrm{d}N - \lambda^{(1)} \left\langle \frac{\partial E}{\partial V} \right\rangle \mathrm{d}V + \lambda^{(1)} \mathrm{d}\langle E \rangle$$

Remembering that we can also calculate dS by combining the first and second laws of thermodynamics (see handout 2) we arrive at:

$$\mathrm{d}S = \frac{P}{T}\mathrm{d}V - \frac{\mu}{T}\mathrm{d}N + \frac{1}{T}\mathrm{d}E$$

Equating coefficients of dE gives us:

$$\lambda^{(1)} = \frac{1}{k_B T} = \beta$$

This quantity $\frac{1}{k_BT}$ appears in many places in statistical mechanics so it is thus given the special symbol β . The canonical partition function is equal to:

$$Z_c(N,V,T) = \sum_i e^{-\beta E_i}$$

where the sum here runs over all microstates that have volume V and number of atoms N. The probability of being in any microstate with volume V and number of atoms N is:

$$p_i = \frac{e^{-\rho E_i}}{Z_c(N, V, T)}$$

By inserting the expression above into $\sum_i p_i$ and differentiating it with respect to β it is possible to show that:

$$\langle E \rangle = \sum_{i} E_{i} p_{i} = -\left(\frac{\partial \ln Z_{c}(N, V, T)}{\partial \beta}\right)$$

and that:

$$\langle (E - \langle E \rangle)^2 \rangle = \left(\frac{\partial^2 \ln Z_c(N, V, T)}{\partial \beta^2} \right)$$

In addition, we can relate the logarithm of the canonical partition function to the Helmholtz free energy using:

$$F(N, V, T) = -k_B T \ln Z_c(N, V, T)$$

Last but not least we can show that the constant volume heat capacity (a response function) is related to the ensemble average of the fluctuations in the internal energy via:

$$C_v = \frac{1}{k_B T^2} \langle (E - \langle E \rangle)^2 \rangle$$

Summary

Closed systems are examined using the canonical ensemble in which the volume and number of atoms are assumed fixed. The canonical partition function is connected to the Helmholtz free energy. The internal energy is calculated as an ensemble average.

Which extensive variables are fixed in the isothermalisobaric ensemble

Give a formula for the isothermalisobaric partition function

Give the probability for being in a particular microstate in the isothermalisobaric ensemble

Which is the appropriate thermodynamic potential to use when considering the behaviour of the isothermalisobaric ensemble

Describe two ways in which one can calculate the ensemble average of the energy/volume

Explain how the isothermal compressibility/heat capacity can be calculated The isothermal-isobaric (NPT) ensemble In statistical mechanics when we develop models for closed systems that can do PV work we use the isothermal-isobaric ensemble. Material cannot be exchanged with closed systems so such systems have constant number atoms. The energy and volume, however, have to be calculated as ensemble averages. Inserting these requirements into the expression for dS that we derived on worksheet 3 we arrive at:

$$\frac{\mathrm{d}S}{k_B} = -\left[\lambda^{(1)} \left\langle \frac{\partial E}{\partial N} \right\rangle + \lambda^{(2)} \left\langle \frac{\partial V}{\partial N} \right\rangle \right] \mathrm{d}N + \lambda^{(1)} \mathrm{d}\langle E \rangle + \lambda^{(2)} \mathrm{d}\langle V \rangle$$

Remembering that we can also calculate dS by combining the first and second laws of thermodynamics (see handout 2) we arrive at:

$$\mathrm{d}S = -\frac{\mu}{T}\mathrm{d}N + \frac{1}{T}\mathrm{d}E + \frac{P}{T}\mathrm{d}V$$

Equating coefficients of dE and dV gives us:

$$\lambda^{(1)} = \frac{1}{k_B T} = \beta \qquad \lambda^{(2)} = \frac{P}{k_B T} = \beta P$$

The isothermal-isobaric partition function is equal to:

$$Z_{ii}(N, P, T) = \sum_{i} e^{-\beta E_{i}} e^{-\beta P V_{i}}$$

where the sum here runs over all microstates that have number of atoms N. The probability of being in any microstate with number of atoms N is:

$$p_i = \frac{e^{-\beta E_i} e^{-\beta P V_i}}{Z_{ii}(N, P, T)}$$

By inserting the expression above into $\sum_i p_i$ and differentiating it with respect to (βP) it is possible to show that:

$$\langle V \rangle = \sum_{i} V_{i} p_{i} = -\left(\frac{\partial \ln Z_{ii}(N, P, T)}{\partial (\beta V)}\right)$$

and that:

$$\langle (V - \langle V \rangle)^2 \rangle = \left(\frac{\partial^2 \ln Z_{ii}(N, P, T)}{\partial (\beta V)^2} \right)$$

In addition, we can relate the logarithm of the isothermal-isobaric partition function to the Gibbs free energy using:

$$G(N, P, T) = -k_B T \ln Z_{ii}(N, P, T)$$

Last but not least we can show that the isothermal compressibility (a response function) is related to the ensemble average of the fluctuations in the volume via:

$$\kappa_T = \frac{1}{k_B T} \frac{1}{\langle V \rangle} \langle (V - \langle V \rangle)^2 \rangle$$

Notice also that we can (still) also relate the ensemble average of the energy to a derivative of the logarithm of the $Z_{ii}(N, P, T)$ with respect to β and that as such the constant pressure heat capacity is related to the fluctuations in the total energy for this ensemble.

Summary

Closed systems that can do PV work are examined using the isothermal-isobaric ensemble only the number of atoms is assumed fixed.

Which extensive variables are fixed in the grand canonical ensemble

Give a formula for the grand canonical partition function

Give the probability for being in a particular microstate in the grand canonical ensemble

Which is the appropriate thermodynamic potential to use when considering the behaviour of the grand canonical ensemble

Describe two ways in which one can calculate the ensemble average of the energy/number of atoms The grand canonical (μVT) ensemble In statistical mechanics when we develop models for open systems that cannot do PV work we use the grand canonical ensemble. PV work cannot be exchanged with such systems so they have constant volume. The number of atoms and the energy, however, have to be calculated as ensemble averages. Inserting these requirements into the expression for dS that we derived on worksheet 3 we arrive at:

$$\frac{\mathrm{d}S}{k_B} = -\left[\lambda^{(1)} \left\langle \frac{\partial E}{\partial V} \right\rangle + \lambda^{(2)} \left\langle \frac{\partial N}{\partial V} \right\rangle \right] \mathrm{d}V + \lambda^{(1)} \mathrm{d}\langle E \rangle + \lambda^{(2)} \mathrm{d}\langle N \rangle$$

Remembering that we can also calculate dS by combining the first and second laws of thermodynamics (see handout 2) we arrive at:

$$\mathrm{d}S = \frac{P}{T}\mathrm{d}V + \frac{1}{T}\mathrm{d}E - \frac{\mu}{T}\mathrm{d}N$$

Equating coefficients of dE and dN gives us:

$$\lambda^{(1)} = \frac{1}{k_B T} = \beta \qquad \lambda^{(2)} = -\frac{\mu}{k_B T} = -\beta\mu$$

The grand canonical partition function is equal to:

$$Z_{gc}(\mu, V, T) = \sum_{i} e^{-\beta E_{i}} e^{\beta \mu N}$$

where the sum here runs over all microstates that have volume V. The probability of being in any microstate with volume V is:

$$p_i = \frac{e^{-\beta E_i} e^{\beta \mu N_i}}{Z_{qc}(\mu, V, T)}$$

By inserting the expression above into $\sum_i p_i$ and differentiating it with respect to $(\beta \mu)$ it is possible to show that:

$$\langle N \rangle = \sum_{i} N_{i} p_{i} = \left(\frac{\partial \ln Z_{gc}(\mu, V, T)}{\partial(\beta \mu)} \right)$$

and that:

$$\langle (N - \langle N \rangle)^2 \rangle = \left(\frac{\partial^2 \ln Z_{gc}(\mu, V, T)}{\partial (\beta \mu)^2} \right)$$

In addition, we can relate the logarithm of the grand canonical partition function to the Grand potential using:

$$\Omega = -k_B T \ln Z_{gc}(\mu, V, T)$$

Notice also that we can (still) also relate the ensemble average of the energy to a derivative of the logarithm of the $Z_{gc}(\mu,V,T)$ with respect to β and that as such we can calculate an unnamed heat capacity from the fluctuations in the total energy for this ensemble.

Summary

Open systems can be examined using the grand-canonical ensemble in which only the volume is assumed fixed. The number of atoms and energy are calculated by ensemble averaging.

How is the canonical partition function connected to the microcanonical partition function

How is the isothermalisobaric partition function connected to the canonical partition function

Hos is the grand canonical partition function connected to the canonical partition function **Relationships between ensembles** We can derive formula that relate the partition functions in the various ensembles. For example, the microcanonical and canonical partition functions are related by:

$$Z_c(N,V,T) = \int Z_{mc}(N,V,E) e^{-\beta E} dE$$

You can arrive at this formula by remembering that the microcanoncial partition function $Z_{mc}(N, V, E)$ is just equal to the number of microstates with number of atoms N, volume V and energy E. Each of these microstates will make a contribution of $e^{-\beta E}$ to the sum in the canonical partition function and hence the total contribution of the $Z_{mc}(N, V, E)$ microstates will be $Z_{mc}(N, V, E)e^{-\beta E}$. The integral can be thought of the continuous limit of a summation and hence the formula above. A similar logic allows one to relate the canonical and isothermal isobaric partition functions using:

$$Z_{ii}(N, P, T) = \int Z_c(N, V, T) e^{-\beta P V} \mathrm{d}V$$

and the grand canonical and canonical by:

$$Z_{gc}(\mu, V, T) = \int Z_c(N, V, T) e^{\beta \mu N} \mathrm{d}N$$

What do we mean when we talk about the term thermodynamic limit

Why is classical thermodynamic recovered in this limit.

The thermodynamic limit We call the limit when the number of atoms goes to infinity $(N \rightarrow \infty)$ the thermodynamic limit. In this limit fluctuations around ensemble averages are zero and consequently all the ensembles are identical. The absence of any fluctuations means that classical thermodynamics (especially Gibbs phase rule) is recovered in this limit.

Summary

Integrals allow us to connect the various partition functions. The thermodynamic limit is the limit as $N \to \infty$. In this limit all ensembles are identical and classical thermodynamics is recovered.