

## Lecture 15

### Physics 404

We will do statistical mechanics with systems that can exchange particles, in addition to energy, with a reservoir. This is called the Grand Canonical Ensemble of statistical mechanics. The first goal is to find the probability that a system will have  $N$  particles and energy  $\varepsilon_s$ . We will work in analogy with the canonical ensemble for systems that exchange energy with a reservoir, where we found the probability

of occupation of a state of energy  $\varepsilon_s$  to be  $P(\varepsilon_s) = \frac{e^{-\varepsilon_s/\tau}}{Z}$ , where  $Z$  is the partition function (see the

Lecture 7 summary). We are now looking for a joint probability that the system has  $N$  particles and energy  $\varepsilon_s$ ,  $P(N, \varepsilon_s)$ .

We assume that the reservoir and system are in equilibrium at temperature  $\tau$  and chemical potential  $\mu$ . This means that they are exchanging energy and particles in dynamic equilibrium, with no net flow of either quantity. The combined reservoir + system is isolated and therefore has a fixed total energy  $U_0$  and fixed total particle number  $N_0$ . If the system has  $N$  particles, then the reservoir has  $N_0 - N$  particles. If the system has energy  $\varepsilon_s$ , then the reservoir has energy  $U_0 - \varepsilon_s$ . If we precisely define the particle number and precise quantum state (list of quantum numbers 's') of the system, then the multiplicity of the reservoir + system is given by that of the reservoir alone, since the state of the system is precisely defined:  $g_{Total} = g_R(N_0 - N, U_0 - \varepsilon_s) \times g_s(N, \varepsilon_s) = g_R(N_0 - N, U_0 - \varepsilon_s) \times 1$ , where  $g$  is the multiplicity of the reservoir or system. Precisely specifying the state of the system means that it has a multiplicity of 1. Hence the probability of finding the system with  $N$  particles and energy  $\varepsilon_s$ ,  $P(N, \varepsilon_s) \propto g_R(N_0 - N, U_0 - \varepsilon_s)$ .

The relative likelihoods of the system being in states  $(N_1, \varepsilon_1)$  vs.  $(N_2, \varepsilon_2)$  is now a ratio of multiplicities for the reservoir:  $\frac{P(N_1, \varepsilon_1)}{P(N_2, \varepsilon_2)} = \frac{g_R(N_0 - N_1, U_0 - \varepsilon_1)}{g_R(N_0 - N_2, U_0 - \varepsilon_2)}$ . We write the multiplicity in terms of the entropy:  $\sigma = \log(g)$ , and then do a Taylor series expansion of the reservoir entropy for small changes in particle number and energy (this is very similar to the flow of lecture 7). The result for the probability ratio is  $\frac{P(N_1, \varepsilon_1)}{P(N_2, \varepsilon_2)} = \frac{\exp[(\mu N_1 - \varepsilon_1)/\tau]}{\exp[(\mu N_2 - \varepsilon_2)/\tau]}$ . The chemical potential  $\mu$  and temperature  $\tau$  arise from the partial derivatives of the entropy with respect to the particle number and energy, respectively. The term  $\exp[(\mu N_1 - \varepsilon_1)/\tau]$  is known as the Gibbs factor. To calculate the probability, we need a normalization factor. In analogy with the partition function  $Z$ , we define the Gibbs sum (aka the grand sum, the grand partition function) as  $\mathcal{Z} = \sum_{N=0} \sum_{\varepsilon_s(N)} e^{(N\mu - \varepsilon_s)/\tau}$ , which is the sum over all possible particle numbers in the system, followed by a sum over all possible states of the  $N$ -particle system. This double sum is sometimes abbreviated "ASN", which stands for "all states and numbers of particles." Note that the number sum starts at  $N = 0$ , which gives a term of the form  $e^{(0\mu - \varepsilon_s(0))/\tau}$ . Ordinarily one takes  $\varepsilon_s(0) = 0$ , which means that the first term in the Gibbs sum is 1. Thus the probability for the system to have  $N$  particles and energy  $\varepsilon_s$  is  $P(N, \varepsilon_s) = \frac{1}{\mathcal{Z}} e^{(N\mu - \varepsilon_s)/\tau}$ . This probability is properly normalized.

The particle number and energy of the system are both fluctuating quantities, not fixed. One can find the thermal average of both of these quantities by playing 'derivative games' with the grand

partition function:  $\langle N \rangle = \tau \frac{\partial \log Z}{\partial \mu} = \lambda \frac{\partial \log Z}{\partial \lambda}$ , where  $\lambda \equiv e^{\mu/\tau}$  is called the absolute activity, and  $U = \langle \epsilon \rangle = \left( \mu \tau \frac{\partial}{\partial \mu} - \frac{\partial}{\partial (1/\tau)} \right) \log Z$ . The higher the chemical potential, the higher the activity  $\lambda$  of the species.

Now consider an interesting example of dopants in a semiconductor like Si. Silicon has a valence of  $(3s)^2(3p)^2$  and crystallizes in the 'diamond structure' in which each Si atom is covalently bonded to each of its 4 nearest neighbors. If an impurity such as P, As, or Sb is added, it goes in as a substitutional defect, impersonating a Si atom. However these dopants have one additional electron and one additional nuclear charge. The dopant atoms form 4 covalent bonds with the neighboring Si atoms, but then have one electron left over. That electron can orbit the dopant nucleus (of charge  $+e$ ) in a hydrogenic orbital. One finds that the binding energy of this hydrogenic state is about 30-50 meV, depending on the dopant atom, and the electron orbits with a 'Bohr radius' of about 3 nm.

We can treat the single dopant atom as the system. The reservoir is the Si crystal. We assume that the system and reservoir are in thermal equilibrium at temperature  $\tau$  and diffusive equilibrium with chemical potential  $\mu$ . They exchange electrons and energy. There are three possible states of the system: 1) The dopant is ionized and the electron is at rest at infinity ( $N = 0, \epsilon = 0$ ), 2) the electron is bound to the dopant ion with spin "up" ( $N = 1, \epsilon = -I$ ), where  $I$  is the binding energy of the electron on the ion (30-50 meV), and 3) the electron is bound to the dopant ion with spin "down" ( $N = 1, \epsilon = -I$ ). In the absence of a magnetic field there is no energy difference between the two bound states. The Gibbs sum is  $Z = \sum_{N=0} \sum_{\epsilon_s(N)} e^{(N\mu - \epsilon_s)/\tau} = \sum_{\epsilon_s(0)} e^{(0\mu - \epsilon_s)/\tau} + \sum_{\epsilon_s(1)} e^{(1\mu - \epsilon_s)/\tau}$ . This becomes  $Z = 1 + 2e^{(\mu+I)/\tau}$ . The probability that the dopant is ionized is given by the ratio of the Gibbs factor for the ionized state to the Gibbs factor:  $P_{\text{ionized}} = \frac{1}{Z} = \frac{1}{1+2e^{(\mu+I)/\tau}}$ . In the limit of low temperature where  $\frac{(\mu+I)}{\tau} \gg 1$ , the ionization probability can be approximated as  $P_{\text{ionized}} \approx \frac{1}{2} e^{-(\mu+I)/\tau} \ll 1$ . This says that doped carriers 'freeze out' of a semiconductor at low temperature.