Thermal Physics - PH441 **John Waczak**
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Free Energy

From Monday we have that $U = \sum_\mu P_\mu E_\mu = -\left(\frac{\partial \ln(Z)}{\partial \beta}\right)_V$. Here is another way to solve for the Free Energy.

$$\begin{aligned}
\Rightarrow d\ln Z &= -Ud\beta + \frac{\partial \ln Z}{\partial V} dV \\
\text{let } \xi &= \frac{\partial \ln Z}{\partial V} \\
d(U\beta) &= Ud\beta + \beta dU \\
\Rightarrow -Ud\beta &= \beta dU - d(U\beta) \\
d\ln Z &= \beta dU - d(U\beta) + \xi dV \\
dU &= \frac{1}{\beta} d(\ln Z - U\beta) + \xi dV \\
&= TdS - pdV = Td(k(\ln Z - U\beta)) + \xi dV \\
\Rightarrow \frac{S}{k} &= \ln Z - \frac{U}{kT} \\
-kT \ln Z &= U - TS = F
\end{aligned}$$

Question: What is F if g μstates all with energy E_0?

$$\begin{aligned}
Z &= \sum_\mu e^{-\beta E_\mu} = g e^{-\beta E_0} \\
F &= -kT\ln(Z) = -kT\ln(ge^{-\beta E_0}) = E_0 - kT\ln(g)
\end{aligned}$$

Note: $F = -kT\ln Z$ is a fine place *to start* as opposed to beginning with $U - -\frac{\partial \ln Z}{\partial \beta}$.

Turning the equation around we have that $Z = e^{-\beta F}$ which can be very useful.

Pressure

Recall that $p = -\frac{\partial U}{\partial V}$ at fixed S from the thermodynamic identity.

Question: How do I fix the entropy?

Recall that $dU = \text{đ}Q - \text{đ}W$ Thus, if we thermally isolate the system, $\text{đ}Q = 0 \Rightarrow dS = 0$ since $T \neq 0$. Another way to think about it is from $S = -k\sum_\mu P_\mu \ln P_\mu$. So if we don't let the probabilities change then $dS = 0$.

Thus, now we have:

$$p = -\frac{\partial U}{\partial V} = -\sum_\mu P_\mu \frac{dE_\mu}{dV} \quad \text{since probabilities are fixed}$$

What do we do with F?

We have two important definitions:

1. $F = -kT \ln Z$
2. $F = U - TS \Rightarrow dF = -SdT - pdV$

This allows us to say that $p = -\frac{\partial F}{\partial V}$ and $S = -\frac{\partial F}{\partial T}$

What is the physics meaning of the Free-energy? Usually you talk about keeping either T or V fixed. For example if you keep the temperature fixed, then F is equal to the work i.e. *the Helmholtz Free energy describes the available work*. Another thing you can say is that it is the energy that is naturally a function of temperature and volume. The internal energy U given by $dU = TdS - pdV$ is naturally a function of entropy and volume.