HH0067 Thermodynamic Identities

In the notes, we would like to understand the chart below:

	$\sigma(U,V,N)$	$U(\sigma,V,N)$	$F(\tau,V,N)$
τ	$\frac{1}{\tau}=\left(\frac{\partial\sigma}{\partial U}\right)_{N,V}$	$\tau=\left(\frac{\partial U}{\partial\sigma}\right)_{N,V}$	×
p	$\frac{p}{\tau}=\left(\frac{\partial\sigma}{\partial V}\right)_{U,N}$	$-p=\left(\frac{\partial U}{\partial V}\right)_{\sigma,N}$	$-p=\left(\frac{\partial F}{\partial V}\right)_{\tau,N}$
μ	$-\frac{\mu}{\tau}=\left(\frac{\partial\sigma}{\partial N}\right)_{U,V}$	$\mu=\left(\frac{\partial U}{\partial N}\right)_{\sigma,V}$	$\mu=\left(\frac{\partial F}{\partial N}\right)_{\tau,V}$

Meanwhile, we also want to show the thermodynamic identities,

$$dU=\tau d\sigma+\mu dN-pdV\ ,\quad dF=-\sigma d\tau+\mu dN-pdV$$

⊘ Legendre transformation.

Recall the transformation from $L(q,\dot q)$ to $H(q,p)$. The variables are defined by the derivatives:
$$p=\frac{\partial L}{\partial\dot q}\ \leftrightarrow\ \frac{\partial H}{\partial p}=\dot q$$
The relation between L & H is

$$\boxed{H(p,q)=p\dot q-L(\dot q,q)}$$

Note that q does not participate the Legendre transform and $\frac{\partial H}{\partial q}=-\frac{\partial L}{\partial q}$.

Now go back to thermal physics. The free energy $F(\tau,V,N)$ can be viewed as Legendre transform of $U(\sigma,V,N)$. The transformed variables $\sigma\leftrightarrow\tau$ are defined by derivatives.

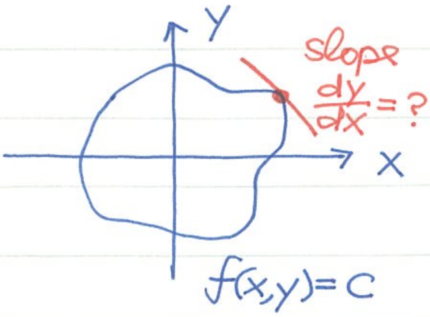
$$\boxed{F=U-\sigma\tau}\qquad \tau=\left(\frac{\partial U}{\partial\sigma}\right)_{N,V}\ \leftrightarrow\ -\sigma=\left(\frac{\partial F}{\partial\tau}\right)_{N,V}$$

Notice that V,N do not participate the Legendre transform and the corresponding derivatives are the same.

$$\boxed{\left(\frac{\partial U}{\partial V}\right)_{\sigma,N}=\left(\frac{\partial F}{\partial V}\right)_{\tau,N}=-p}\quad\text{and}\quad\boxed{\left(\frac{\partial U}{\partial N}\right)_{\sigma,N}=\left(\frac{\partial F}{\partial N}\right)_{\tau,N}=\mu}$$

⊘ Entrop derivatives

The entropy derivatives $\partial\sigma/\partial U$, $\partial\sigma/\partial V$, $\partial\sigma/\partial N$ can be related to τ, p, μ. To establish the relations, let's review the math trick to evaluate the slope of a 2D curve.



$$\frac{dy}{dx} = -\frac{\frac{\partial f}{\partial x}}{\frac{\partial f}{\partial y}}$$ for the curve $f(x,y)=C$.

Rewriting the familiar formula in thermal physics form:
$$\boxed{\left(\frac{\partial y}{\partial x}\right)_f = -\frac{(\partial f/\partial x)_y}{(\partial f/\partial y)_x}}$$

Now apply it to the case —

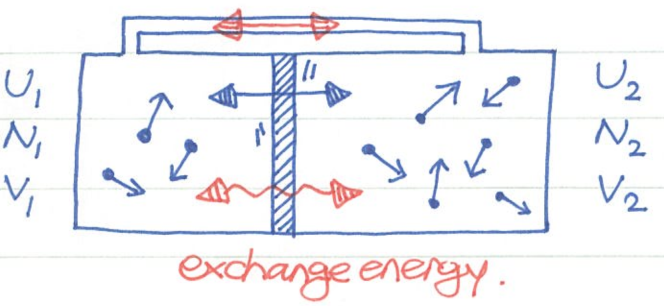
$f \to U$, $x \to V$, $y \to \sigma$
$$\left(\frac{\partial \sigma}{\partial V}\right)_U = -\frac{\left(\frac{\partial U}{\partial V}\right)_\sigma}{\left(\frac{\partial U}{\partial \sigma}\right)_V} = \frac{p}{\tau}$$

Similarly, we can also choose a different set of variables,

$f \to U$, $x \to N$, $y \to \sigma$
$$\left(\frac{\partial \sigma}{\partial N}\right)_U = -\frac{\left(\frac{\partial U}{\partial N}\right)_\sigma}{\left(\frac{\partial U}{\partial \sigma}\right)_V} = -\frac{\mu}{\tau}$$

⊘ Equilibrium criteria revisited.

Consider two systems in thermal and diffusive contacts. In addition, their volumes V_1, V_2 can change as well but the total volume $V = V_1 + V_2$ is constant. What's is the most straight forward derivation for all equilibrium criteria? Well, maximize the entropy $\sigma = \sigma_1 + \sigma_2$ with the constraints $U_1 + U_2 = \text{Const}$, $N_1 + N_2 = \text{Const}$, $V_1 + V_2 = \text{Const}$.



$\boxed{d\sigma = 0} \longrightarrow d\sigma_1 + d\sigma_2 = 0$

simplify by using contraints.

$$\left(\frac{\partial \sigma_1}{\partial U_1} dU_1 + \frac{\partial \sigma_1}{\partial N_1} dN_1 + \frac{\partial \sigma}{\partial V_1} dV_1\right) + \left(\frac{\partial \sigma_2}{\partial U_2} dU_2 + \frac{\partial \sigma_2}{\partial N_2} dN_2 + \frac{\partial \sigma_2}{\partial V_2} dV_2\right) = 0$$

$$\left(\frac{\partial\sigma_1}{\partial U_1}-\frac{\partial\sigma_2}{\partial U_2}\right)dU_1+\left(\frac{\partial\sigma_1}{\partial N_1}-\frac{\partial\sigma_2}{\partial N_2}\right)dN_1+\left(\frac{\partial\sigma_1}{\partial V_1}-\frac{\partial\sigma_2}{\partial V_2}\right)dV_1=0$$

Because U, N, V are independent variables, the above equation leads to three criteria for reaching equilibrium:

$$\boxed{\begin{aligned}\frac{\partial\sigma_1}{\partial U_1}&=\frac{\partial\sigma_2}{\partial U_2}\;\rightarrow\;\frac{1}{\tau_1}=\frac{1}{\tau_2}\\ \frac{\partial\sigma_1}{\partial N_1}&=\frac{\partial\sigma_2}{\partial N_2}\;\rightarrow\;-\frac{\mu_1}{\tau_1}=\frac{\mu_2}{\tau_2}\\ \frac{\partial\sigma_1}{\partial V_1}&=\frac{\partial\sigma_2}{\partial V_2}\;\rightarrow\;\frac{p_1}{\tau_1}=\frac{p_2}{\tau_2}\end{aligned}}$$

Combining all criteria together, we reach the equilibrium conditions: $\tau_1=\tau_2$, $\mu_1=\mu_2$ and $p_1=p_2$. Very reasonable indeed ☺

⊘ Total differentials

Consider the entropy $\sigma(U,V,N)$ with its natural variables.

$$d\sigma=\left(\frac{\partial\sigma}{\partial U}\right)dU+\left(\frac{\partial\sigma}{\partial V}\right)dV+\left(\frac{\partial\sigma}{\partial N}\right)dN$$

I drop all subindices for clarity ☺

$$=\frac{1}{\tau}dU+\frac{p}{\tau}dV-\frac{\mu}{\tau}dN$$

$$\rightarrow\;\boxed{dU=\tau d\sigma+\mu dN-pdV}$$

Energy change comes from THREE different ways: heat, particle and work.

Since there is no approximation involved in deriving the total differential, you can derive the same identity by taking derivative to $U(\sigma,V,N)$ directly.

the same ☺

$$dU=\frac{\partial U}{\partial\sigma}d\sigma+\frac{\partial U}{\partial N}dN+\frac{\partial U}{\partial V}dV=\tau d\sigma+\mu dN-pdV.$$

We can also derive the total differential for the Helmholtz free energy $F(\tau,V,N)$. Note that its natural variables are τ, V, N.

$$dF=\frac{\partial F}{\partial\tau}d\tau+\frac{\partial F}{\partial N}dN+\frac{\partial F}{\partial V}dV=-\sigma d\tau+\mu dN-pdV$$

Let's try to derive the same identity from $F = U - \tau\sigma$

$$dF = dU - \sigma d\tau - \tau d\sigma = \cancel{\tau d\sigma} + \mu dN - p dV - \sigma d\tau - \cancel{\tau d\sigma}$$

$$= -\sigma d\tau + \mu dN - p dV$$ ← the same

You may wonder whether we can obtain the same result if we mess up the natural variables, $F(\tau, V, N) = F(\tau(\sigma), V, N)$

$$dF = \left(\frac{\partial F}{\partial \sigma}\right)_{N,V} d\sigma + \left(\frac{\partial F}{\partial N}\right)_{\sigma,V} dN + \left(\frac{\partial F}{\partial V}\right)_{\sigma,N} dV$$

note that $F = U - \tau\sigma$

$$\left(\frac{\partial F}{\partial \sigma}\right)_{N,V} = \cancel{\left(\frac{\partial U}{\partial \sigma}\right)_{N,V}} - \left(\frac{\partial \tau}{\partial \sigma}\right)_{N,V} \sigma - \cancel{\tau} = -\sigma \left(\frac{\partial \tau}{\partial \sigma}\right)_{N,V}$$

$$\left(\frac{\partial F}{\partial N}\right)_{\sigma,V} = \left(\frac{\partial U}{\partial N}\right)_{\sigma,V} - \sigma \left(\frac{\partial \tau}{\partial N}\right)_{\sigma,V} = \mu - \sigma \left(\frac{\partial \tau}{\partial N}\right)_{\sigma,V}$$

$$\left(\frac{\partial F}{\partial V}\right)_{\sigma,N} = \left(\frac{\partial U}{\partial V}\right)_{\sigma,N} - \sigma \left(\frac{\partial \tau}{\partial V}\right)_{\sigma,N} = -p - \sigma \left(\frac{\partial \tau}{\partial V}\right)_{\sigma,N}$$

Combine all terms together in dF.

$$dF = -\sigma \left[\left(\frac{\partial \tau}{\partial \sigma}\right)_{N,V} d\sigma + \left(\frac{\partial \tau}{\partial N}\right)_{\sigma,V} dN + \left(\frac{\partial \tau}{\partial V}\right)_{\sigma,N} dV \right] + \mu dN - p dV$$

$$= -\sigma d\tau + \mu dN - p dV$$ ← still the same result !!

Now you should have confidence in these thermodynamic identities, no matter which way you derive them

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