Thermodynamics Homework
MAT 561

Christopher Bay

March 6, 2007

Let $\mathbb{V}$ be the 4-dimensional vector space with linear coordinates T, S, p, V, i.e.

$$\mathbb{V} = \mathbb{R}_T \oplus \mathbb{R}_S \oplus \mathbb{R}_p \oplus \mathbb{R}_V$$

where each coordinate has the appropriate physical units. Endow $\mathbb{V}$ with the symplectic form

$$\omega = dT \wedge dS - dp \wedge dV.$$

1. We use ω to identify $\mathbb{R}_p = (\mathbb{R}_V)^*$ via the linear isomorphism

$$\omega_p : \mathbb{R}_p \to (\mathbb{R}_V)^*, \ \partial_p \mapsto \iota(\partial_p)\omega = -dV = -V. \tag{1}$$

Let $U \in C^\infty(\mathbb{R}_S \oplus \mathbb{R}_V)$ be the internal energy. Our goal is to compute the Legendre transform $\mathcal{L}_V U : \mathbb{R}_S \oplus (\mathbb{R}_V)^* \to \mathbb{R}$ of U along the V direction and reinterpret it as a map $\mathbb{R}_S \oplus \mathbb{R}_p \to \mathbb{R}$. Let $s \in \mathbb{R}_S$ and $\alpha \in (\mathbb{R}_V)^*$, and let $U_s : \mathbb{R}_V \to \mathbb{R}$ be the function $U_s(v) = U(s, v)$. Interpret $dU_s : \mathbb{R}_V \to \mathbb{R}_V \times (\mathbb{R}_V)^*$ as a map from $\mathbb{R}_V$ to $(\mathbb{R}_V)^*$ and suppose that this map is a diffeomorphism for each $s \in S$. Then

$$\begin{aligned} \mathcal{L}_V U(s,\alpha) &= \mathcal{L}U_s(\alpha) & (2)\\ &= \langle \alpha, (dU_s)^{-1}(\alpha)\rangle - U(s, (dU_s)^{-1}(\alpha)). & (3) \end{aligned}$$

Here $\langle\ ,\ \rangle : (\mathbb{R}_V)^* \otimes \mathbb{R}_V \to \mathbb{R}$ denotes the canonical pairing. Consider the bilinear map $p \cdot V : \mathbb{R}_p \oplus \mathbb{R}_V \to \mathbb{R}$. Via the diffeomorphism $(dU_s)^{-1} : (\mathbb{R}_V)^* \to \mathbb{R}_V$ we can interpret $p \cdot V$ as a map on $\mathbb{R}_p \oplus (\mathbb{R}_V)^*$ (which is no longer linear, and depends on the choice of $s \in S$). Furthermore, the map ω_p allows us to consider this map as a function on $\mathbb{R}_p$ alone. Making the dependance on s explicit, we have a map $p \cdot V : \mathbb{R}_S \oplus \mathbb{R}_p \to \mathbb{R}$. For $s \in S$ and $\rho \in \mathbb{R}_p$ we have

$$\begin{aligned} p \cdot V(s,\rho) &= p(\rho) \cdot V((dU_s)^{-1}(\omega_p(\rho)))\\ &= (p(\rho)V)((dU_s)^{-1}(\omega_p(\rho)))\\ &= \langle p(\rho)V, (dU_s)^{-1}(\omega_p(\rho))\rangle\\ &= -\langle \alpha, (dU_s)^{-1}(\alpha)\rangle, \end{aligned}$$

where $\alpha := \omega_p(\rho) \in (\mathbb{R}_V)^*$, and the minus sign is due to the sign in (**??**). Now, we may also interpret the term on the far right of (**??**) as a function $U : \mathbb{R}_S \oplus \mathbb{R}_p \to \mathbb{R}$ via ω_p:

$$U(s,\rho) = U(s, (dU_s)^{-1}(\omega_p(\rho))) = U(s, (dU_s)^{-1}(\alpha)).$$

Therefore,

$$-\mathcal{L}_V U = pV + U = H \in C^\infty(\mathbb{R}_S \oplus \mathbb{R}_p),$$

where H is the enthalpy.

For a path γ, the change in enthalpy along γ is

$$\int_\gamma dH = \int_\gamma dU + \int_\gamma (pdV + Vdp).$$

According to the First Law of Thermodynamics,

$$\int_\gamma dU = W(\gamma) + Q(\gamma) = -\int_\gamma pdV + Q(\gamma).$$

Thus, the change in enthalpy is $Q(\gamma) + \int_\gamma Vdp$ and the change in enthalpy is equal to the heat added precisely when $\int_\gamma Vdp = 0$. In particular, this occurs for isobaric (constant pressure) processes.

2. The form ω also induces an isomorphism

$$\omega_T : \mathbb{R}_T \to (\mathbb{R}_S)^*, \ \partial_T \mapsto \iota(\partial_T)\omega = dS = S. \tag{4}$$

We now derive the relationship

$$-\mathcal{L}_S U = U - TS = F_{Helm} \in C^\infty(\mathbb{R}_T \oplus \mathbb{R}_V)$$

where the $U - TS$ term will be properly interpreted.

We assume that for each $v \in V$ the map dU_v is a diffeomorphism. By definition, for $\sigma \in (\mathbb{R}_S)^*$ and $v \in V$,

$$\begin{aligned} \mathcal{L}_S U(\sigma, v) &= \mathcal{L}U_v(\sigma) & (5)\\ &= \langle \sigma, (dU_v)^{-1}(\sigma)\rangle - U((dU_v)^{-1}(\sigma), v). & (6) \end{aligned}$$

The bilinear map $TS : \mathbb{R}_T \oplus \mathbb{R}_S \to \mathbb{R}$ can be considered as a map on $\mathbb{R}_T \oplus (\mathbb{R}_S)^*$ (which also depends on v) by precomposing with $(dU_v)^{-1} : (\mathbb{R}_S)^* \to \mathbb{R}_S$ in the second argument. It can then be considered as a map on $\mathbb{R}_T$ by precomposing with ω_T in the second argument. We then have a map $TS : \mathbb{R}_T \oplus \mathbb{R}_V \to \mathbb{R}$, given by

$$\begin{aligned} TS(t, v) &= T(t)S((dU_v)^{-1}(\omega_T(t))) \\ &= \langle T(t)S, (dU_v)^{-1}(\omega_T(t))\rangle \\ &= \langle \sigma, (dU_v)^{-1}(\sigma)\rangle, \end{aligned}$$

where $\sigma := \omega_T(t) \in (\mathbb{R}_S)^*$. The U term in (**??**) may be interpreted as a map $U \in C^\infty(\mathbb{R}_T \oplus \mathbb{R}_V)$ as follows:

$$U(t, v) = U((dU_v)^{-1}(\omega_T(t)), v) = U((dU_v)^{-1}(\sigma), v).$$

Therefore,

$$-\mathcal{L}_S U = U - TS = F_{Helm} \in C^\infty(\mathbb{R}_T \oplus \mathbb{R}_V).$$

For a path γ the change in F_{Helm} along γ is

$$\int_\gamma dF_{Helm} = \int_\gamma dU - \int_\gamma (SdT + TdS).$$

By the First Law of Thermodynamics,

$$\int_\gamma dU = W(\gamma) + Q(\gamma) = W(\gamma) + \int_\gamma TdS.$$

So the change in F_{Helm} is $W(\gamma) - \int_\gamma SdT$ and the change in the Helmholtz free energy is equal to the work done by the system precisely when $\int_\gamma SdT = 0$. In particular, this occurs for isothermal (constant temperature) processes.

3. Now use ω to identify $\mathbb{R}_p \oplus \mathbb{R}_T = (\mathbb{R}_S \oplus \mathbb{R}_V)^*$ via $\omega_p \oplus \omega_T$. Suppose $dU : \mathbb{R}_S \oplus \mathbb{R}_V \to (\mathbb{R}_S \oplus \mathbb{R}_V)^*$ is a diffeomorphism. Then for $\sigma \in (\mathbb{R}_S)^*$ and $\nu \in (\mathbb{R}_V)^*$,

$$\mathcal{L}U(\sigma, \nu) = \langle (\sigma, \nu), (dU)^{-1}(\sigma, \nu)\rangle - U((dU)^{-1}(\sigma, \nu)).$$

In the notation used above,

$$dU(s, v) = \frac{\partial U}{\partial S} \mid_{(s,v)} dS + \frac{\partial U}{\partial V} \mid_{(s,v)} dV = dU_v(s) + dU_s(v),$$

so that $dU(s, v) = (dU_v(s), dU_s(v))$. So $dU(s, v) = (\sigma, \nu)$ implies $(dU)^{-1}(\sigma, \nu) = ((dU_v)^{-1}(\sigma), (dU_s)^{-1}(\nu))$ where the pair (s, v) which depends on the pair (σ, ν). Then for some (s, v) we have

$$\mathcal{L}U(\sigma, \nu) = \langle \sigma, (dU_v)^{-1}(\sigma)\rangle + \langle \nu, (dU_s)^{-1}(\nu)\rangle - U((dU_v)^{-1}(\sigma), (dU_s)^{-1}(\nu)).$$

Since (s, v) depends on $(\sigma, \nu) \in (\mathbb{R}_S \oplus \mathbb{R}_V)^*$ the interpretations made above are still valid, but now the first term is $TS \in C^\infty((\mathbb{R}_S \oplus \mathbb{R}_V)^*)$ and the second term is $-pV \in C^\infty((\mathbb{R}_S \oplus \mathbb{R}_V)^*)$. For example, if $t = \omega_T^{-1}(\sigma)$ then

$$\begin{aligned} \langle \sigma, (dU_v)^{-1}(\sigma)\rangle &= \langle \omega_T(t), (dU_v)^{-1}(\sigma)\rangle \\ &= \langle T(t)S, (dU_v)^{-1}(\sigma)\rangle \\ &= T(\omega_T^{-1}(\sigma))S((dU_v)^{-1}(\sigma)) \end{aligned}$$

and similarly for $-pV$. By precomposing with $(\omega_p \oplus \omega_T)^{-1}$ we have $TS, -pV, U \in C^\infty(\mathbb{R}_p \oplus \mathbb{R}_T)$ and

$$-\mathcal{L}U = U - TS + pV = F_{Gibbs} \in C^\infty(\mathbb{R}_p \oplus \mathbb{R}_T).$$