Exercise sheet 2

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Contents

1 problem 1 - Thermodynamic Potentials and State Variables

1.1 (a, 2P)

show:

$$\left(\frac{\partial f}{\partial u}\right)_v \left(\frac{\partial u}{\partial f}\right)_v = 1 \tag{1}$$

we may write:

$$u = f^{-1}\left(f(u)\right) \tag{2}$$

with that we can write for the differential

$$du = df^{-1} = \left(\frac{\partial f^{-1}}{\partial f}\right)_v \left(\frac{\partial f}{\partial u}\right)_v du = \left(\frac{\partial u}{\partial f}\right)_v \left(\frac{\partial f}{\partial u}\right)_v du \tag{3}$$

by comparing the l.h.s with the r.h.s we get:

$$\boxed{\left(\frac{\partial u}{\partial f}\right)_v \left(\frac{\partial f}{\partial u}\right)_v = 1 \qquad \square} \tag{4}$$

show:

$$\left(\frac{\partial f}{\partial u}\right)_v \left(\frac{\partial u}{\partial v}\right)_f \left(\frac{\partial v}{\partial f}\right)_u = -1 \tag{5}$$

to start we write down the differential forms of u and f:

$$df = \left(\frac{\partial f}{\partial u}\right)_v du + \left(\frac{\partial f}{\partial v}\right)_u dv \tag{6}$$

$$du = \left(\frac{\partial u}{\partial f}\right)_v df + \left(\frac{\partial u}{\partial v}\right)_f dv \tag{7}$$

Combining these two, we may write:

$$
\begin{aligned}
df &= \left(\frac{\partial f}{\partial u}\right)_v \left(\left(\frac{\partial u}{\partial f}\right)_v df + \left(\frac{\partial u}{\partial v}\right)_f dv\right) + \left(\frac{\partial f}{\partial v}\right)_u dv && (8)\\
&= \underbrace{\left(\frac{\partial f}{\partial u}\right)_v \left(\frac{\partial u}{\partial f}\right)_v}_{=1\ \textit{(from eq. 4)}} df + \left(\frac{\partial f}{\partial u}\right)_v \left(\frac{\partial u}{\partial v}\right)_f dv + \left(\frac{\partial f}{\partial v}\right)_u dv && (9)
\end{aligned}
$$

Now we can reorder and multiply by $\left(\frac{\partial v}{\partial f}\right)_u$ and we get:

$$
\begin{aligned}
\left(\frac{\partial f}{\partial u}\right)_v \left(\frac{\partial u}{\partial v}\right)_f dv &= -\left(\frac{\partial f}{\partial v}\right)_u dv && (10)\\
\left(\frac{\partial v}{\partial f}\right)_u \left(\frac{\partial f}{\partial u}\right)_v \left(\frac{\partial u}{\partial v}\right)_f dv &= \underbrace{\left(\frac{\partial v}{\partial f}\right)_u \left(\frac{\partial f}{\partial v}\right)_u}_{=1} dv && (11)\\
&= -1\, dv && (12)
\end{aligned}
$$

By comparing the l.h.s. with the r.h.s. we get

$$
\boxed{\left(\frac{\partial f}{\partial u}\right)_v \left(\frac{\partial u}{\partial v}\right)_f \left(\frac{\partial v}{\partial f}\right)_u = -1 \qquad \square \qquad (13)}
$$

1.2 (b, 1P)

Relate: The isochoric pressure change $\left(\frac{\partial p}{\partial T}\right)_V$ to the standard response functions:

$$
\begin{aligned}
\alpha &= \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p && (14)\\
\kappa &= -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T && (15)
\end{aligned}
$$

We start writing down the differentials for p and V:

$$
\begin{aligned}
dp &= \left(\frac{\partial p}{\partial V}\right)_T dV + \left(\frac{\partial p}{\partial T}\right)_V dT && (16)\\
dV &= \left(\frac{\partial V}{\partial p}\right)_T dp + \left(\frac{\partial V}{\partial T}\right)_p dT && (17)
\end{aligned}
$$

By multiplying dV in the differential with $\left(\frac{\partial p}{\partial V}\right)_T$, we can combine dp and dV to:

$$
0 = \left[\left(\frac{\partial p}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p + \left(\frac{\partial p}{\partial T}\right)_V\right] dT \qquad (18)
$$

and finally:

$$\boxed{\left(\frac{\partial p}{\partial T}\right)_V = -\left(\frac{\partial V}{\partial p}\right)_T^{-1}\left(\frac{\partial V}{\partial T}\right)_p = \frac{\alpha}{\kappa}} \tag{19}$$

1.3 (c,d 2P)

Express: The differential forms of the caloric states $U(p,T)$ and $U(V,T)$, by standard response functions.

We write down the differentials for the caloric states:

$$dU = \left(\frac{\partial U}{\partial p}\right)_T dp + \left(\frac{\partial U}{\partial T}\right)_p dT \tag{20}$$

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_p dT \tag{21}$$

We will use the expression for Gibbs and Helmholtz free energy:

$$G = G(p,T) = U - TS + pV = Vdp - SdT \tag{22}$$

$$F = F(V,T) = U - TS = -pdV - SdT \tag{23}$$

and the Maxwell relation

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V \tag{24}$$

This relation holds since:

$$\left(\frac{\partial S}{\partial V}\right)_T = -\left(\frac{\partial^2 F}{\partial T \partial V}\right) = -\left(\frac{\partial^2 F}{\partial V \partial T}\right) = \left(\frac{\partial p}{\partial T}\right)_V \qquad \square \tag{25}$$

We want to express the partial derivatives in eq. 20 and 21.

i:$(\frac{\partial U}{\partial V})_T$

V and T are the natural variables of the Helmholtz free energy F. Using eq. 23 yields:

$$\left(\frac{\partial F}{\partial V}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T - T\left(\frac{\partial S}{\partial V}\right)_T \quad // \left(\frac{\partial T}{\partial V}\right)_T = 0 \text{ obviously} \tag{26}$$

comparing the partial derivatif of F on the l.h.s. with eq. 23 and replacing the second term of the r.h.s by its Maxwell relation (eq. 24), we may write:

$$-p = \left(\frac{\partial U}{\partial V}\right)_T - T\left(\frac{\partial p}{\partial T}\right)_V \tag{27}$$

$$\implies \left(\frac{\partial U}{\partial V}\right)_T = \underbrace{-p + T\left(\frac{\partial p}{\partial T}\right)_V}_{\text{for part d}} = -p + T\frac{\alpha}{\kappa_T} \tag{28}$$

Where the last step follows from solution of part 1.2b.

ii: $\left(\frac{\partial U}{\partial T}\right)_V$

We will again use F, since we have the same variables as before. Taking the partial derivative yields:

$$\left(\frac{\partial F}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V - S - T\left(\frac{\partial S}{\partial T}\right)_V \tag{29}$$

Now we want to find an expression for the last term on the r.h.s.. We can infer:

$$\left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial T}{\partial S}\right)_V^{-1} = \left(\frac{\partial^2 U}{\partial S \partial S}\right)^{-1} = \frac{1}{T}\theta_V^{-1} \tag{30}$$

where,

$$\theta_V := \frac{1}{T}\left(\frac{\partial^2 U}{\partial S \partial S}\right)_V \tag{31}$$

Comparing the partial derivatif of F on the l.h.s. with eq. 23 we may write:

$$\left(\frac{\partial U}{\partial T}\right)_V = \frac{1}{\theta_V} = C_V \tag{32}$$

iii: $\left(\frac{\partial U}{\partial p}\right)_T$

We will look at Gibbs free energy, since p and T are it's natural variables. We may write:

$$\left(\frac{\partial G}{\partial p}\right)_T = \left(\frac{\partial U}{\partial p}\right)_T - T\left(\frac{\partial S}{\partial p}\right)_T + V + p\left(\frac{\partial V}{\partial p}\right)_T \tag{33}$$

Using the same strategy as from above, we can easily identify $\left(\frac{\partial G}{\partial p}\right)_T = V$. The last term is related by eq. 15 to the response function κ_T. So we only have to determine one term. We may write:

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial^2 G}{\partial T \partial p}\right) = -\left(\frac{\partial^2 G}{\partial p \partial T}\right) = -\left(\frac{\partial V}{\partial T}\right)_p = -V\alpha \tag{34}$$

Where we applied eq. 14 in the last step. Now we have:

$$\left(\frac{\partial U}{\partial p}\right)_T = (\kappa_T p - \alpha T)V \tag{35}$$

iv: $\left(\frac{\partial U}{\partial T}\right)_p$

Since we have the same variables here as for the case iii, we will look again on the Gibbs free energy:

$$\left(\frac{\partial G}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_p - S - T\left(\frac{\partial S}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p \tag{36}$$

Using the same strategies as above, we may immediately write:

$$- S = \left(\frac{\partial U}{\partial T}\right)_p - S - T\left(\frac{\partial S}{\partial T}\right)_p + pV\alpha \tag{37}$$

The last term arises by usage of eq. 14. Let us identify the missing term:

$$\left(\frac{\partial S}{\partial T}\right)_p = \left(\frac{\partial T}{\partial S}\right)_p^{-1} = \left(\frac{\partial^2 U}{\partial S \partial S}\right)^{-1} = \frac{1}{T}\theta_p^{-1} \tag{38}$$

where,

$$\theta_p := \frac{1}{T}\left(\frac{\partial^2 U}{\partial S \partial S}\right)_p \tag{39}$$

With this, we have:

$$\left(\frac{\partial U}{\partial T}\right)_p = \frac{1}{\theta_p} - PV\alpha = C_p - pV\alpha \tag{40}$$

Collecting the expressions for the partial derivatives of U from equations 28, 32, 35 and 40, we may finally write:

$$\boxed{\begin{aligned} dU_{V,T} &= \left(T\frac{\alpha}{\kappa_T} - p\right) dV + C_V\,dT && (41) \\ dU_{p,T} &= (\kappa_T - \alpha T)\, V\,dp + (C_p - pV\alpha)\,dT && (42) \end{aligned}}$$