Exercise sheet 3

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Contents

1 problem 1 - Einstein relations

(a) compute: The fluctuation parameter matrix:

$$\mathbf{g} = \begin{pmatrix} g_{UU} & g_{UV} \\ g_{UV} & g_{VV} \end{pmatrix} \tag{1}$$

and

(b) show: The following relations:

$$\left(\frac{\partial T}{\partial V}\right)_U = \frac{1}{C_V}\left(\frac{\alpha}{\kappa_T}T - p\right) \tag{2}$$

$$\left(\frac{\partial p}{\partial V}\right)_U = -\frac{1}{\kappa_T V} + \frac{\alpha}{\kappa_T C_V}\left(\frac{\alpha}{\kappa_T}T - p\right) \tag{3}$$

(a) To compute g_{UU}, we use the relation from the lecture:

$$g_{UU} = -\left(\frac{\partial}{\partial U}\right)_V \left(\frac{\partial}{\partial U}\right)_V S(U,V) \tag{4}$$

$$= -\left(\frac{\partial}{\partial U}\right)_V \left(\frac{\partial S}{\partial U}\right)_V \tag{5}$$

$$= -\left(\frac{\partial}{\partial U}\right)_V T^{-1} \tag{6}$$

$$= \frac{1}{T^2}\left(\frac{\partial T}{\partial U}\right)_V \tag{7}$$

$$= \frac{1}{C_V T^2} \tag{8}$$

Where we used the differential of S:

$$dS = \left(\frac{\partial S}{\partial U}\right)_V dU + \left(\frac{\partial S}{\partial U}\right)_V dV \tag{9}$$

$$= \frac{1}{T}dU + \frac{p}{T}dV \tag{10}$$

and the definition of the isochoric heat capacity $C_V = \left(\frac{\partial U}{\partial T}\right)_V$. We will proceed analog for the other cases:

$$g_{UV} = -\left(\frac{\partial}{\partial U}\right)_V \left(\frac{\partial}{\partial V}\right)_U S \tag{11}$$

$$= -\left(\frac{\partial}{\partial V}\right)_U \left(\frac{\partial S}{\partial U}\right)_V \tag{12}$$

$$= \frac{1}{T^2}\left(\frac{\partial T}{\partial V}\right)_U \tag{13}$$

$$= \frac{1}{T^2 C_V}\left(\frac{\alpha}{\kappa_T}T - p\right) \tag{14}$$

And finally

$$g_{VV} = -\left(\frac{\partial}{\partial V}\right)_U \left(\frac{\partial}{\partial V}\right)_U S \tag{15}$$

$$= -\left(\frac{\partial}{\partial V}\right)_U \left(\frac{\partial S}{\partial V}\right)_U \tag{16}$$

$$= -\left(\frac{\partial}{\partial V}\right)_U \frac{p}{T} \tag{17}$$

$$= -\frac{1}{T}\left(\frac{\partial p}{\partial V}\right)_U + \frac{p}{T^2}\left(\frac{\partial T}{\partial V}\right)_U \tag{18}$$

$$= \frac{1}{\kappa_T V T} - \frac{\alpha}{\kappa_T C_V}\left(\frac{\alpha}{\kappa_T}T - p\right) + \frac{p}{T^2 C_V}\left(\frac{\alpha}{\kappa_T}T - p\right) \tag{19}$$

$$= \frac{1}{\kappa_T V T} + \frac{1}{C_V}\left(\frac{p}{T^2} - \frac{\alpha}{\kappa_T}\right)\left(\frac{\alpha}{\kappa_T}T - p\right) \tag{20}$$

(b) We use the relation for dU derived in exercise sheet 1, problem 1c (eq. 42):

$$dU_{V,T} = \left(T\frac{\alpha}{\kappa_T} - p\right) dV + C_V dT \tag{21}$$

we want to find $\left(\frac{\partial T}{\partial V}\right)_U$. From eq. 21 we get for $dU = 0$,

$$\left(\frac{\alpha}{\kappa_T}T - p\right) dV = C_V dT \tag{22}$$

$$\Rightarrow \left.\frac{dT}{dV}\right|_{U=\text{const}} = \left(\frac{\partial T}{\partial V}\right)_U = \frac{1}{C_V}\left(\frac{\alpha}{\kappa_T}T - p\right) \tag{23}$$

To show eq. 3, we use the relation $\left(\frac{\partial F}{\partial V}\right)_T = -p$. With this we may write:

$$\begin{aligned}
\left(\frac{\partial p}{\partial V}\right)_U &= -\left(\frac{\partial}{\partial V}\right)_U \left(\frac{\partial}{\partial V}\right)_T F && (24)\\
&= -\left(\frac{\partial}{\partial V}\right)_T \left(\frac{\partial}{\partial V}\right)_U U + \left(\frac{\partial}{\partial V}\right)_T \left(\frac{\partial}{\partial V}\right)_U (TS) && (25)\\
&= \left(\frac{\partial}{\partial V}\right)_T \left(S\left(\frac{\partial T}{\partial V}\right)_U + T\left(\frac{\partial S}{\partial V}\right)_U\right) && (26)\\
&= \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial T}{\partial V}\right)_U + \left(\frac{\partial p}{\partial V}\right)_T && (27)\\
&= \left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_U + \left(\frac{\partial V}{\partial p}\right)_T^{-1} && (28)\\
&= \frac{\alpha}{\kappa_T}\frac{1}{C_V}\left(\frac{\alpha}{\kappa_T}T - p\right) - \frac{1}{V\kappa_T} && (29)
\end{aligned}$$