

### [tex37] Coexistence line of continuous phase transition

Consider 1 mol of a fluid with two phases 1 and 2 in coexistence. The coexistence line is  $p(T)_{coex}$ . Suppose that the volume  $V$  and the entropy  $S$  vary continuously at the transition ( $\Delta S = 0$  and  $\Delta V = 0$ ), but the response functions  $C_p$  (heat capacity at constant pressure),  $\alpha_p$  (thermal expansivity), and  $\kappa_T$  (isothermal compressibility) are discontinuous. Now consider the differentials  $dS$  and  $dV$  for each phase and for paths in the  $(T, p)$ -plane. Then calculate  $\Delta S \doteq dS^{(2)} - dS^{(1)}$  and  $\Delta V \doteq dV^{(2)} - dV^{(1)}$  between points an infinitesimal distance across the coexistence line

- (a) at constant  $p$ ,
- (b) at constant  $T$ .

In the limit where the distance between the two points shrinks to zero, the ratio  $\Delta S/\Delta V$  stays finite and expresses (via Clausius-Clapeyron) the slope  $(dp/dT)_{coex}$  of the coexistence line in terms of the discontinuities,  $\Delta C_p, \Delta \alpha_p, \Delta \kappa_T$ , in the response functions.

(c) Derive a relation between  $\Delta C_p, \Delta \alpha_p, \Delta \kappa_T$  from the consistency condition of the results obtained in parts (a) and (b).

**Solution:**