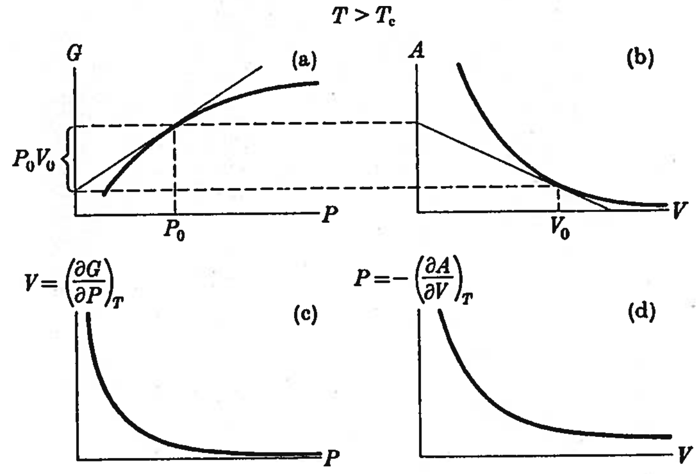

FIG. 2.4. Geometrical interpretation of the relation between the Gibbs and Helmholtz potentials at a fixed temperature $T > T_c$. This construction, adapted from Morse (1969) and Griffiths (unpublished lecture notes), is based on the identities $A = G - PV$ and $V = (\partial G/\partial P)_T$. The vertical distance between the dashed lines in (a) and (b) is the product PV, and on subtracting this from G we obtain A. Note that the construction indicated is unambiguous because $G(T, P)$ is a concave function of P (for all P) and $A(T, V)$ is a convex function of V (for all V). Also shown are the volume as a function of pressure (obtained from the pressure derivative of $G(T, P)$) and the pressure as a function of volume (obtained from the volume derivative of $A(T, V)$).

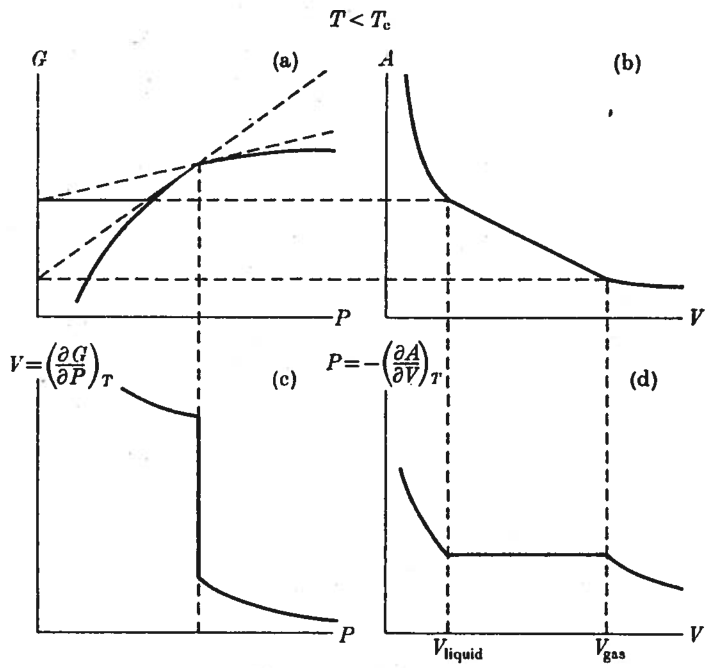

FIG. 2.5. The Gibbs and Helmholtz potentials for a fixed temperature $T < T_c$, where T_c is the transition temperature for a first-order phase transition. Also shown are the volume as a function of pressure and the pressure as a function of volume. Note that the value of the pressure at which the volume discontinuity occurs is not the critical pressure P_c but rather the value of the saturated vapour pressure $P_{sat}(T)$ given by the vapour pressure curve of Fig. 1.1a. Thus the system is seen to undergo a *first-order* transition on crossing the vapour pressure curve at constant temperature T ($T < T_c$).

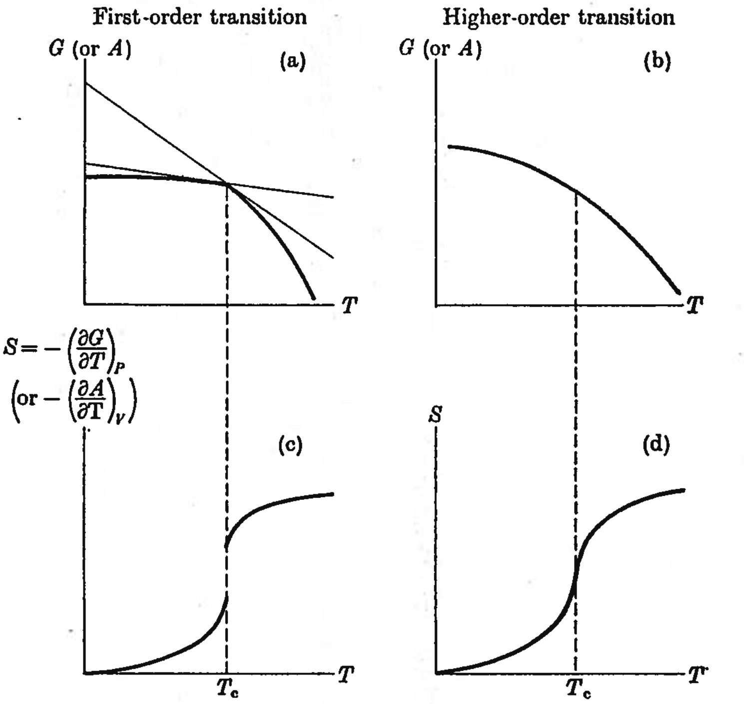

Fig. 2.6. (a) Temperature dependence of either the Gibbs potential at fixed pressure or the Helmholtz potential at fixed volume. The system shown undergoes a phase transition at $T = T_c$, accompanied by a latent heat (entropy discontinuity). (b) Same as (a) except that the phase transition has no latent heat. (c)–(d) show the entropy obtained from the temperature derivative of A or G. For this particular example, $C \sim dS/dT$ appears to diverge at T_c for both the first-order and the higher-order transition.

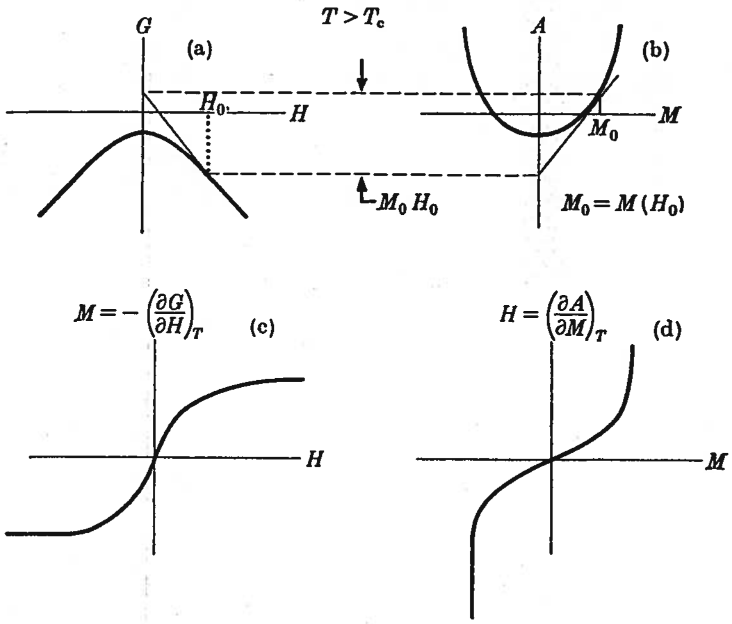

FIG. 2.8. Geometrical relation between $G(T, H)$ and $A(T, M)$ for a fixed temperature $T > T_c$. Also shown are the magnetization as a function of field (obtained from $M = -(\partial G/\partial H)_T$) and the field as a function of magnetization (obtained from $H = (\partial A/\partial M)_T$).

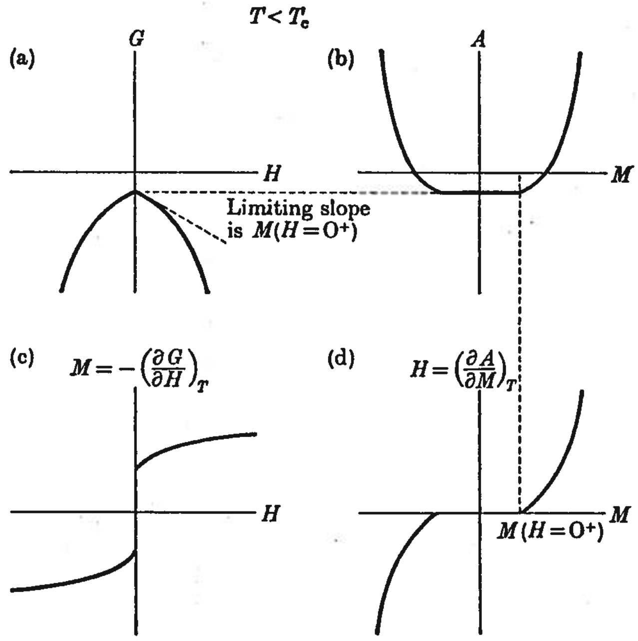

FIG. 2.9. Relation between $G(T, H)$ and $A(T, M)$ for a fixed temperature $T < T_c$. Also shown are the M–H isotherms (obtained from $G(T, H)$) and the H–M isotherms (obtained from $A(T, M)$).