

# Negative heat capacities and first order phase transitions

L. G. Moretto, J. B. Elliott, L. Phair and G. J. Wozniak

Nuclei have long been associated with liquids, as testified by the success of the liquid drop model. The surface energy introduces the simplest correction to the bulk, leading to a model of 1% accuracy. A similar approach may hold for other kinds of clusters for which the surface energy is the main correction to bulk properties.

The equilibrium between a liquid and its vapor is described by the Clapeyron Equation  $dp/dT = \Delta H_m/\Delta V_m T$ ,  $p$  and  $T$  are the pressure and temperature,  $\Delta H_m$  is the molar enthalpy of vaporization and  $\Delta V_m$  is the difference of the molar volumes of vapor,  $V_m^v$ , and liquid,  $V_m^l$ . Specialization to the case of a drop of radius  $r$ , described readily in the thermodynamic limit [1], is achieved by modifying the enthalpy to account for the surface energy [2]

$$\Delta H_m = \Delta H_m^0 - c_s S_m^l = \Delta H_m^0 - \frac{3c_s V_m^l}{r}, \quad (1)$$

$\Delta H_m^0$  is the bulk molar enthalpy,  $S_m^l$  and  $V_m^l$  are the surface and volume of the drop and  $c_s$  is the surface energy coefficient.

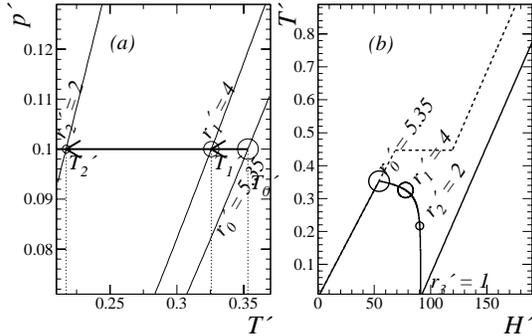


Figure 1: (a) Saturated vapor pressure as a function of  $T$ . (b) Isobaric caloric curve: dashed (solid) lines represent bulk (drop) behavior.  $H' = H(\Delta H_m^0/3c_s V_m^l)^3/(4\pi/V_m^l)$ .

Neglecting  $V_m^l$  compared to  $V_m^v$ , considering the vapor ideal ( $V_m^v = T/p$ ) and assuming  $\Delta H_m$

constant we integrate the Clapeyron Equation,

$$p = p_0 \exp[-(\Delta H_m^0/T) + (3c_s V_m^l/rT)]. \quad (2)$$

This contains all thermodynamical information needed to characterize the phase coexistence of the liquid drop of with its vapor. Fig. 1a gives a map of  $p' = p'(T', r')$  ( $p' = p/p_0$ ,  $T' = T/\Delta H_m^0$ ,  $r' = r\Delta H_m^0/3c_s V_m^l$ ). The salient feature is the rise of  $p$  with decreasing  $r$ . For any  $r$ , Eq. (2) describes the equilibrium between the drop and its vapor; it is the phase diagram of the drop where a *phase* is defined by  $r$ .

To operate at constant pressure  $p_0$ , the drop is enclosed in a deformable container and an external pressure  $p_0$  is applied. As the drop is heated  $T$  increases via  $\Delta H = C_p^l \Delta T$ ,  $C_p^l$  is the liquid's heat capacity and is nearly constant. When  $T$  reaches  $T_0$  and  $p = p_0$ , the vapor first appears and expands against the container. The heat of vaporization is absorbed at a rate  $H_m(r_0)$  and as the drop evaporates,  $r$  decreases from its initial value  $r'_0$ . At constant  $T$ ,  $p$  would rise, but at constant  $p$ ,  $T$  decreases (Fig. 1a) as the system absorbs its heat of vaporization, thus,

$$\begin{aligned} \Delta H &\propto \frac{1}{3}(r_0'^3 - r'^3) - \frac{1}{2}(r_0'^2 - r'^2), \\ T' &= T'_0[(1 - r'^{-1})/(1 - r_0'^{-1})]. \end{aligned} \quad (3)$$

After the drop has fully evaporated, the vapor's temperature increases via  $\Delta H = C_p^v \Delta T$ ,  $C_p^v$  is the vapor's heat capacity at constant pressure. The caloric curve (Eq. (3), Fig. 1b) has a decreasing branch associated with the phase transition along which the heat capacity will be negative!

## References

- [1] L. Rayleigh, Phil. Mag. **34**, 94 (1917).
- [2] L. G. Moretto, *et al.*, Phys. Rep. **287**, 249 (1997).