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The origin of predicted and observed anomalies in caloric curves of nuclei and other mesoscopic systems is investigated. It is shown that a straightforward thermodynamical treatment of an evaporating liquid drop leads to a backbending in the caloric curve and to negative specific heats in the two phase coexistence region. The cause is found not in the generation of additional surface, but in the progressive reduction of the drop’s radius, and surface, with evaporation.

The thermodynamical equilibrium properties of first order phase transitions are completely describable in terms of the thermodynamic state variables associated with the individual separate phases. This is not the case in continuous phase transitions, where the two phases become progressively more similar as the critical point is approached. For this reason, in contrast with continuous phase transitions, first order phase transitions are “trivial,” and interesting only in so far as they herald the appearance of a hitherto unknown or undescribed phase.

Renewed attention to phase transitions has been generated by studies of models with well defined Hamiltonians with either short range interactions (e.g. the Ising model [1-5] or the lattice gas model [6-13]) or incorporating long range interactions such as gravitation or electromagnetic interactions [10,14-19]. Several of these studies, microcanonical and canonical, were performed numerically, thus the results apply directly to finite (mesoscopic) systems. Features expected to disappear in the thermodynamic limit, if such a limit exists, were noticed and were claimed to be essential, characteristic indicators of phase transitions in mesoscopic systems [12,13,20-29]. For instance, first order phase transitions were associated with anomalous convex intruders in the entropy versus energy curves, resulting in backbendings in the caloric curve, and in negative heat capacities [5,12,13,20-31].

It is often claimed that these features appear only in microcanonical calculations and are thought to become lost or smeared out in the haze of canonical calculations [5,20-22,25,26]. These anomalies have been attributed to a variety of causes, the foremost of which are surface effects, and long range forces [20,24-26]. Unfortunately however, the numerical nature of the calculations tends to make the identification of the causes of negative heat capacities rather problematic.

In the context of nuclear physics, microcanonical models of nuclear multifragmentation have associated the anomalies of a convex intruder with the onset of multifragmentation [20,25,26]. Furthermore, lattice gas models in the isobaric regime have also shown negative specific heats in the coexistence region, where multifragmentation also appears [12,13]. The question of whether the two transitions are related and possibly coincident with the liquid-vapor transition is still very much open.

Recently, the claim has been made of an empirical observation of these anomalies, such as negative heat capacities in nuclear systems [31]. These negative heat capacities have been inferred from the study of fluctuations in multifragmenting nuclear systems. Thus there is interest in elucidating the origin of such anomalies in models as well as experiments.

In particular, it would be highly desirable to ground any evidence for these anomalies, theoretical or otherwise, on thermodynamics itself, minimally modified to allow for the possible role of surface effects related to the finiteness of the system.

In this paper we illustrate analytically how effects such as negative heat capacities can arise within a standard thermodynamical treatment. We consider the evaporation of a drop of ordinary liquid. Our only concern with mesoscopicity is the explicit treatment of the surface of the drop.

Nuclear systems have long been associated with liquids, as testified by the success of the liquid drop model. In the spirit of the liquid drop model, the surface energy introduces the simplest (and dominant!) correction to the bulk energy, leading to a one percent model in systems as small as 40 nucleons and possibly smaller. A similar approach should hold for other kinds of clusters for which the surface energy may also be the first and dominant correction to the bulk properties. Specifically, we will study the role of surface in generating the anomalies in the caloric curve.

A “mesoscopic” system, such as a tiny drop of liquid with radius \( r \) can be readily described in the pure thermodynamic limit [32-36]. The complete analogy between the liquid-vapor phase coexistence of a liquid in the bulk and for a drop can be seen in Fig. 1, where the molar free energy \( F_m \) at constant temperature is plotted versus molar volume \( V_m \) for the two phases. The two free energy branches, for liquid and for vapor, can be considered completely independent. No interaction is assumed between the two phases. Coexistence becomes possible...
in the region of volume \( V \) where the overall free energy can be minimized through the common tangent construction. The equilibrium pressure of the saturated vapor is immediately given by

\[
p = -\frac{\partial F}{\partial V} \bigg|_T.
\]

No qualitative difference in the picture results by considering a drop of finite radius \( r \). The only difference is that the overall free energy of the drop (solid curves) as we shall see below, is higher than that of the bulk (dashed curves) and the equilibrium vapor pressure is correspondingly higher.

The state of equilibrium between a liquid and its vapor can be described in the simplest way by the Clapeyron Equation

\[
\frac{dp}{dT} = \frac{\Delta H_m}{\Delta V_m T}.
\]

where, \( p \) 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 \( r \) can be achieved by modifying the enthalpy to account for the surface energy \[37\]

\[
\Delta H_m = \Delta H_m^0 - c_s V_m^l = \frac{3c_s V_m^l}{r}
\]

where \( \Delta H_m^0 \) is the “bulk” molar enthalpy, \( c_s \) and \( V_m^l \) are the surface and volume of the drop and \( c_s \) is the surface energy coefficient.

Neglecting \( V_m^l \) compared to \( V_m^v \) and considering the vapor ideal, i.e. \( V_m^v = T/p \), we can integrate Eq. (2), assuming also \( \Delta H_m \) to be constant. We obtain

\[
p = p_0 \exp\left(-\frac{\Delta H_m^0}{T} + \frac{3c_s V_m^l}{rT}\right)
\]

or

\[
p = p_{\text{bulk}} \exp\left(\frac{3c_s V_m^l}{rT}\right).
\]

This equation contains all the thermodynamical information necessary to characterize the phase coexistence of the liquid drop of radius \( r \) with its vapor. The salient feature is the rise of the vapor pressure with decreasing radius. Fig. 2 gives a map of the function \( p' = p'(T, r') \), in terms of the scaled variables

\[
p' = \frac{p}{p_0}, \quad T' = \frac{T}{\Delta H_m^0}, \quad r' = \frac{\Delta H_m^0}{3c_s V_m^l r}.
\]

For any given radius \( r \), the function \( p = p(T, r) \) describes the equilibrium condition between the drop and its vapor. In other words, it is the phase diagram of the drop. The drop appears here as a “phase” defined by its radius \( r \). A change in radius implies a change in phase.
with $C_p^v$ is the liquid’s heat capacity and is approximately constant. When $T$ reaches the value $T_0$ at which the vapor pressure $p(r_0) = p_0$, the vapor first appears and it expands against the container. The heat of vaporization is absorbed at a rate $H_m(r_0)$. However, as it evaporates, the drop sees its radius decreasing from its initial value, chosen to be $r_0^* = 5.35$. At constant temperature the vapor pressure would rise, but, at constant pressure, as we are now operating, the temperature decreases as shown in Fig. 2, as the system absorbs its heat of vaporization, so that,

$$\Delta H = \int_{r}^{r_0} \Delta H_m \frac{dV}{V_{m}^{l}}$$

$$= 4\pi \left( \frac{3c_s V_{m}^{l}}{\Delta H_{m}^{l}} \right)^3 \left[ \frac{1}{3} (r_0^3 - r^3) - \frac{1}{2} (r_0^2 - r^2) \right] \quad (8)$$

and

$$T' = T_0 \left( \frac{1 - \frac{r'}{r_0}}{1 - \frac{r_0'}{r_0}} \right) \quad (9)$$

After the drop has totally evaporated, the vapor can increase its temperature according to

$$\Delta H = C_p^v \Delta T \quad (10)$$

where $C_p^v$ is the vapor heat capacity at constant pressure. The resulting caloric curve defined parametrically by Eq. (8) and Eq. (9) and shown in Fig. 3 is rather interesting. It has a decreasing branch associated with the phase transition, along which the heat capacity is negative! (See Fig. 4.)

As an aside we note that the scaled radius $r'$ is just the ratio of the bulk energy to the surface energy. Thus for a nuclear system the range shown: $1 \leq r_0' \leq 5.35$, corresponds to a gold nucleus ($A = 197$) evaporating to a single nucleon.

These rather extraordinary features are wholly due to the interesting but, in a way, accidental history of the deceasing radius with increasing evaporation.

Because of the surface energy effect, each drop, of a given radius $r_0$, is a separate phase in and of itself, different from that associated with a different radius $r_1$. At fixed radius $r_0$, nothing anomalous appears in Fig. 2; the pressure versus temperature curve, caloric curve and heat capacity are all perfectly normal. Anomalies arise when the system drifts from one radius to another, or from one phase to another.

Typically, experiments [38-42] and calculations [5,12,13,20-31] heat a preassigned system with a certain amount of energy $\Delta E$ or $\Delta H$, and determine the resulting change in entropy $S$ and temperature $1/T = \partial S/\partial E$; from the resulting caloric curve, phase coexistence diagrams are extracted. However, as shown above, the evolution of the system occurring during heating introduces complications in the construction of a phase diagram from such a caloric curve.

To avoid this problem an experimentalist or theorist would have to keep the radius constant or correct for its change while determining the vapor pressure as a function of the temperature, thereby eliminating the accidental aspects associated with the evolution of the system. The proper representation of all the thermophysical properties associated with the coexistence liquid drop-vapor is that given in Eq. (4) and Fig. 2.

The results obtained here are firmly grounded on thermodynamics with a straightforward accounting of finiteness through the surface correction. They are exact in the limit in which the liquid drop model holds, namely, down to nuclei/clusters containing 20 or so constituents. They are completely general, as they do not depend on specific details of the system but rather on its gross properties. In fact, they should be used as the paragon for lattice gas models and the like. In the limit in which these models represent liquid vapor coexistence, they must reproduce the present results.

Even more importantly, this approach obviates the need for repeating numerical calculations for each individual system or drop size. All that is required is to determine the bulk energy (enthalpy) and the surface energy coefficient of a give phase once and for all.

It is not clear to us at the moment if the transition studied here and the anomalies associated with it have a direct counterpart in the allegedly observed phase transition in nuclear systems [31]. It is however worth repeating that, once the constraint of constant pressure is enforced, the results described here are entirely general, as they apply to any small system undergoing solid-vapor or liquid vapor transitions.

Anomalies in the heat capacities observed in microcanonical calculations have been attributed to the
increase in surface generated as additional liquid-vapor interface, e.g. in the formation of bubbles [26]. In the present case, however, and possibly generally, this conclusion is not valid. In a finite system undergoing a liquid-vapor transition there is on average a decrease of surface as the evaporation proceeds. Any interior vapor bubble formation is disfavored by a Boltzmann factor \( \exp(-\Delta V/T) \), compared to the location of the same vapor on the outside of the drop, whose surface area ends up actually decreasing. Thus, the resulting anomalies are indeed surface related, but in a very different way.

Several conclusions and warnings can be drawn from this treatment of an evaporating liquid drop:

1. Mesoscopic systems can be dealt with within the context of standard thermodynamics, minimally modified to include the surface.

2. Anomalous features such as a backbending caloric curve and attending negative heat capacities can be made to appear by allowing the system to "evolve" in parameter space (e.g. \( r \)).

3. These features appear in a strict thermodynamically treatment and thus are not specific features of microcanonicity.

4. These features are, in a way, accidental. They reflect the evolution of the system in parameter space (here, the radius \( r \)). If the radius is kept fixed and the system is confined to a "single" liquid phase, the phase coexistence diagrams are completely ordinary, and no new thermodynamics is evident.
