

Mesoscopy and thermodynamics

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Abstract. The interplay of thermodynamics and statistical mechanics is discussed with special attention to mesoscopic systems and phase transitions.

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1 Introduction

Thermodynamics is an empirical science devoted to the description of macroscopic systems. It follows formally from its three principles and stands firmly independent of any microscopic description. Statistical mechanics, on the other hand, is founded on the general principles of mechanics, and attempts to bridge the gap from the microscopic description of a system to its macroscopic thermodynamical properties. This attempt has met with undeniable success through the introduction of ensembles such as microcanonical, canonical, grand canonical, etc., whereby microstates, constrained to satisfy some specific macroscopic conditions are used to obtain average values of macroscopic variables. Its success, however, must be measured in terms of its agreement with thermodynamics, which is the final judge. Thus the potentially unbridled

course of theoretical speculation is wisely trimmed by the correctness of thermodynamical empiricism.

The “recent” extension of experimental [1–3] and theoretical research to systems that are neither wholly microscopic nor macroscopic, thus aptly named mesoscopic, should be enlightened by the same wisdom. While names and functions (temperature, entropy, free energy. . .) were borrowed from thermodynamics, the urge to label the field as “novel” led to rash statements such as the primacy of one ensemble (microcanonical) over the others, or even to the affirmation of a “new” thermodynamics or to the “failure” of the “old” thermodynamics and its principles.

These rash statements have often been accompanied by a cavalier disregard for the physical definitions and identification of phases, claiming the presence of phase transitions on the basis of possibly myopic interpretations of anecdotal numerical results.

The resulting rush to calculate properties of a plethora of individual mesoscopic systems underscores the essential limitations of these efforts, which renounce the beautiful generality of thermodynamics for results as limited and specific as the systems under consideration become legion. This direction leads to as many individual “statistical mechanics” as there are mesoscopic systems. We shall discuss this point further and suggest a natural solution.

The study of numerical rather than analytical methods has given rise to two different problems. On one hand, the size of the system is finite, on the other, the choice of the algorithm becomes of paramount significance.

The first problem, which leads to the need of extrapolating correctly to the thermodynamic limit, is a negative aspect of these numerical computations. On the other hand, the ever increasing importance of microscopic systems in experimental and applied science, makes the finite size of great interest in itself, and the attending differences from the thermodynamic limit are drawing ever increasing attention. The second problem is related to the first. Some algorithms strive to compute the partition function versus temperature (in the canonical approach), while others try to compute the entropy versus energy (the microcanonical approach). A lot of discussion has arisen concerning the merits of the two approaches, in particular with regards to the observation of interesting anomalies and to the extrapolation to the thermodynamic limit.

In the struggle between the two camps, the upper hand seems to be taken by the microcanonical algorithms which just generate and count configurations in phase space at

any given energy. The result of these calculations is the level density $\rho(E)$ as a function of energy, or, equivalently, the entropy $S(E)$ as a function of energy. Anomalies appear in the dependence of $S(E)$ on E , like regions of constant slope, negative first derivatives and positive second derivatives (concave intruders). The elementary nature of this procedure seems to ward off any confusion.

Yet the transition from microcanonical to the more commonly used canonical language and variables becomes dangerous and misleading in correspondence to the very anomalies for which one is searching. Thus the resulting negative temperature, negative specific heat, etc. tend to create misunderstanding and confusion.

Our own approach uses the reductionistic device of describing the plethora of mesoscopy in terms of the “old” thermodynamics, which is augmented by the least number of new quantities necessary to describe the finiteness of the systems. This idea, of course, is not new. It is embodied, for instance, in the “liquid drop” model, so much successful in nuclear physics. It consists of expanding thermodynamic functions such as the free energy in terms of a “finiteness” variable $A^{-1/3}$ where A is the “size - mass” of the finite system. So we write:

$$F(A, T) = a_v(T)A + a_s(T)A^{2/3} + a_c A^{1/3} + \dots \quad (1)$$

where $a_v(T)$, $a_s(T)$, $a_c(T)$ are the temperature T dependent volume, surface, curvature, etc. free energy coefficients. The leading term is the extensive volume term $a_v(T)A$, the others (which can be shape dependent, e.g. $a_s(T) = a_s^0(T)f(s/s_0)$ where s is the actual surface s of the object and s_0 is the surface of its equivalent sphere)

are the terms that account for finiteness and vanish for $A \rightarrow \infty$. The shape variables can either be fixed, or let free to assume the value demanded by the free energy minimization. The fact that in the nuclear case the expansion can be safely stopped at the surface term while retaining accuracies of the order of one percent down to sizes as small as $A = 20$ gives us the hope that just by adding a surface term we may obtain similarly adequate descriptions for many other mesoscopic systems. Furthermore, for short range forces it happens that the surface coefficient is nearly equal and opposite to the volume coefficient, i.e. $a_v(T) = -a_s(T)$. This leads to a great deal of economy and to an extreme generality.

It is important to appreciate that in any calculation applied to mesoscopic systems, the presence of the surface as a physical boundary, and boundary condition is of paramount importance for all calculations. Many of the claimed novel and general features resulting from finite system calculations are either strongly dependent on such boundary conditions, or are artifacts of unwittingly introduced boundary conditions which may not have necessarily any specific physical meaning.

We shall exemplify the above ideas by considering phase coexistence and phase transitions.

2 Microcanonical and canonical worlds and their languages

The microcanonical world is conceptually the simplest one. It deals with an ensemble of totally isolated systems.

The lack of particle or energy exchange with the environment makes the calculational aspect particularly transparent. Literally one counts the number of configurations of the system for a narrow energy interval around any given energy; that is the level density at that energy. Its logarithm is the entropy, now the “thermodynamic” potential in terms of V , N and E . That is all there is to do. However, measurements typically deal with the canonical world of temperature T and variables depending on T .

Consequently one takes the derivative of entropy with respect to energy and calls that the inverse temperature

$$\frac{\partial S}{\partial E} = \beta = \frac{1}{T}. \quad (2)$$

From this equation other quantities like the caloric curve $E = E(T)$ and specific heat $C_V = \left. \frac{\partial E}{\partial T} \right|_V$ are determined. But it is here that problems arise. Equation (2) is a macroscopic thermodynamic relationship. But what is its microscopic origin? And does it apply all the time? In the following we consider this in detail.

2.1 The transformation from energy scale to temperature scale

We are going to perform this transformation in two equivalent ways: the first more physical, the second more formal.

Let us consider a microcanonical system fully characterized by the relationship

$$\rho = \rho(E), S = S(E). \quad (3)$$

Let us put a small system (thermometer) with a few degrees of freedom (e.g. a classical one dimensional harmonic oscillator) into contact with the microcanonical system.

Any energy state ε of the thermometer is associated with a probability $p(\varepsilon)$ equal to the degeneracy of the microcanonical system at energy $E - \varepsilon$

$$p(\varepsilon) \simeq \rho(E - \varepsilon)\rho_T(\varepsilon) \quad (4)$$

where the level density of the one dimensional harmonic oscillator $\rho_T(\varepsilon)$ is constant. Given the “smallness” of the thermometer, ε is microscopically small compared to the “macroscopic” energy E . So the following Taylor expansion is in order

$$\ln p(\varepsilon) = \ln \rho(E) - \varepsilon \frac{\partial \ln \rho}{\partial E} \Big|_{\varepsilon=0} + \frac{1}{2} \varepsilon^2 \frac{\partial^2 \ln \rho}{\partial E^2} \Big|_{\varepsilon=0} - \dots \quad (5)$$

But

$$\frac{\partial \ln \rho}{\partial E} = \frac{\partial S}{\partial E} = \frac{1}{T}, \quad (6)$$

$$\frac{\partial^2 \ln \rho}{\partial E^2} = -\frac{1}{T^2 C_V} \quad (7)$$

and

$$p(\varepsilon) = \rho(E) \exp\left(-\frac{\varepsilon}{T} - \frac{1}{T^2 C_V} \varepsilon^2 - \dots\right). \quad (8)$$

Assuming the second term of the expansion to be small, the population of the energy state of a thermometer is given by a Boltzmann factor, uniquely characterized by the “temperature” T , which, without more ado can be attributed to our microcanonical system. The quantity C_V , thermodynamically identifiable with the heat capacity of the system, is macroscopically large making the truncation of the expansion to the linear term reasonable.

More formally, let us consider the relationship between microcanonical and canonical ensembles in terms of the relationship between partition function \mathcal{Z} and level density ρ . The partition function is given by

$$\mathcal{Z}(\beta) = \sum_i \exp(-\beta E_i) = \int_0^\infty \rho(E) \exp(-\beta E) dE. \quad (9)$$

The independent variable β is the inverse of the canonical temperature T . In the canonical world at constant β (T), the microcanonical world at constant E is represented as a weighted sum, the weight being a Boltzmann factor.

Equation (9) transforms the microcanonical world of energy E and level density $\rho(E)$ in to the canonical world of temperature $T = \frac{1}{\beta}$ and partition function $\mathcal{Z}(\beta)$. This transformation is a Laplace transform.

Notice that for any given T or β there is a *distribution of energies*, and not a single value. The distribution in E is the integrand of Eq. (9)

$$p(E) = \rho(E) \exp(-\beta E) = A \exp\left(-\frac{(E - E_0)^2}{2\sigma^2}\right). \quad (10)$$

This distribution is usually sharply peaked. The maximum is given by

$$\frac{\partial \ln p}{\partial E} = \frac{\partial \ln \rho}{\partial E} - \beta = 0 \quad (11)$$

or

$$\frac{\partial \ln \rho}{\partial E} = \frac{1}{T} \quad (12)$$

which, for any T , can be solved for the most probable value of E .

The variance in E is given by

$$\frac{1}{\sigma^2} = \frac{\partial^2 \ln \rho}{\partial E^2} = \frac{1}{T^2 C_V} \quad (13)$$

or

$$\Delta E = T \sqrt{C_V}. \quad (14)$$

Where C_V is again the heat capacity.

Since $E \propto N \propto C_V$, $\Delta E \propto \frac{1}{\sqrt{N}}$ and becomes negligible in the thermodynamic limit of $N \rightarrow \infty$. In order to go from the canonical to the microcanonical world we need

to invert Eq. (10). The inverse Laplace transform is

$$\rho(E) = \frac{1}{2\pi i} \oint \mathcal{Z}(\beta) \exp(\beta E) d\beta. \quad (15)$$

Again, the microcanonical world is an integral over a distribution of the canonical worlds, and a given value of the microcanonical energy corresponds to a distribution in β or T given by the integrand of Eq. (15). The inverse transform is an integral in the complex plane. Under ordinary circumstances (to be defined), the integrand has a saddle point located at a coordinate β_0 defined by

$$\frac{\partial \ln \mathcal{Z}}{\partial \beta} + E = 0 \quad (16)$$

or

$$E = -\frac{\partial \ln \mathcal{Z}}{\partial \beta}. \quad (17)$$

For any given E one can solve Eq. (16) for β_0 . The right hand side of Eq. (17) can be reduced to a Gaussian integral

$$\rho(E) = \frac{1}{2\pi i} \mathcal{Z}(\beta_0) \exp(\beta_0 E) \int_{-i\infty}^{+i\infty} \exp\left(-\frac{(\beta - \beta_0)^2}{2\sigma^2}\right) id\beta \quad (18)$$

where

$$\frac{1}{\sigma_\beta^2} = -\frac{\partial^2 \ln \mathcal{Z}}{\partial \beta^2} = -\frac{\partial E}{\partial \beta} = -\frac{\partial E}{\partial T} \frac{\partial T}{\partial \beta} = C_V T \quad (19)$$

or

$$\sigma_\beta^2 = \frac{1}{C_V T^2}. \quad (20)$$

This β -variance can be transformed into a T -variance

$$\sigma_T^2 = \frac{T^2}{C_V} \quad (21)$$

or

$$\Delta T = \frac{T}{\sqrt{C_V}}. \quad (22)$$

The fluctuations in T decrease as $\frac{1}{\sqrt{N}}$ and vanish in the thermodynamic limit. Everything appears very normal and stable. Yet something may go terribly wrong in transforming microcanonical results into a canonical world.

3 Microcanonical anomalies and canonical disasters

3.1 Negative temperatures

Let us begin with a simple model: a chain of N links. One unit of energy is necessary to break one link. Microcanonically the energy is

$$E = n \quad (23)$$

where n is the number of broken links.

The level density parameter is

$$\rho = \frac{N!}{n!(N-n)!}. \quad (24)$$

The level density and the entropy have a maximum for $n = \frac{N}{2}$, so the temperature

$$\frac{1}{T} = \frac{\partial S}{\partial n} \quad (25)$$

goes from 0 to ∞ as n goes from 0 to $\frac{N}{2}$ and from $-\infty$ to 0 as n goes from $\frac{N}{2}$ to N . We are faced with a “negative” temperature!

Canonically we have

$$\mathcal{Z} = \sum_0^N \frac{N!}{n!(N-n)!} \exp(-\beta n) = (1 + \exp(-\beta))^N. \quad (26)$$

The energy is

$$E = -\frac{\partial \ln \mathcal{Z}}{\partial \beta} = \frac{N \exp(-\beta)}{1 + \exp(-\beta)} = n. \quad (27)$$

Despite our prejudice that temperatures ought to be positive, everything seems to be well behaved by generalizing the range of β (and T) from $-\infty$ to $+\infty$.

Furthermore, it can be seen from Eq. (15) that there is a saddle point in the complex plane. The Gaussian approximation is legitimate since C_V is positive throughout

the range of β , and the contour integral can be evaluated by the method of steepest descents, yielding

$$\rho = \frac{N^N}{(N-n)^{N-n} n^n} / \sqrt{2\pi \frac{n(N-n)}{N}}. \quad (28)$$

Not surprisingly this is the Stirling approximation to Eq. (24) and it is exceedingly precise from $0 < n \leq N$. Therefore, nothing prevents the translation from microcanonical to canonical world in the entire energy range, even if this costs us the intuitive feeling that there ought not to be negative temperatures.

Even if everything looks nice and stable, let us try to put a thermometer into contact with our system. Equation (8) is reported below

$$\rho(E - \varepsilon) = \rho(e) \exp\left(-\frac{\varepsilon}{T} - \frac{\varepsilon^2}{T^2 C_V}\right). \quad (29)$$

If T is negative, clearly there is no convergence. Energy will be drawn into the thermometer which will probably explode. We call this first order divergence.

3.2 Negative specific heat

The simplest model with negative specific heat that comes to mind is a very interesting one: the hydrogen atom. The energy levels are given by

$$E_n = R \left(1 - \frac{1}{n^2}\right) \quad (30)$$

where R is the Rydberg constant. The degeneracy is

$$\sum_{l=0}^{n-1} (2l+1) = n^2. \quad (31)$$

The above level spacing, including the degeneracy is

$$\frac{\partial E}{\partial n} = \frac{2R}{n^3} \frac{1}{n^2} \quad (32)$$

and the level density is

$$\rho \simeq \frac{\partial n}{\partial E} \simeq \frac{n^5}{2R} \simeq \frac{1}{2R} \left(-\frac{R}{E-R}\right)^{\frac{5}{2}}. \quad (33)$$

The entropy is

$$S \simeq \ln \rho \simeq \frac{3}{2} \ln R - \ln 2 - \frac{5}{2} \ln(R-E). \quad (34)$$

The ‘‘temperature’’ is

$$\beta = \frac{1}{T} = \frac{\partial S}{\partial E} = \frac{5}{2} \frac{1}{R-E} \quad (35)$$

or

$$T = \frac{2}{5}(R-E). \quad (36)$$

This strange temperature is maximal at $E \sim 0$ ($T = \frac{2}{5}R$) and decreases linearly with E and vanishes at the ionization limit $E = R$.

The heat capacity is

$$C_V = -\frac{5}{2} \quad (37)$$

These results seem (and are!) counter intuitive. Is there anything wrong? The analysis is fine, up to the evaluation of the entropy. The problems begin when we proceed to calculate the temperature.

In order to see what the problems are, we must go back to our two ways of going from the microcanonical to the canonical world.

3.2.1 First method

Let us put a thermometer (a classical one dimensional harmonic oscillator) in contact with our system. The resulting energy distribution of the thermometer is

$$p(\varepsilon) = p(E - \varepsilon) = \rho(E) \exp\left(-\frac{E}{T} - \frac{\varepsilon^2}{T^2 C_V} - \dots\right). \quad (38)$$

This expansion must converge to be meaningful.

This requires that

$$0 < T \ll E, C_V \gg 1 \left(0 < T \sim \frac{E}{N} \ll E, C_V \sim N \right). \quad (39)$$

If these considerations are met, in other words if T is microscopic and C_V is macroscopic, then the expansion can be stopped at the first term, the quantity T is well defined and can be used as an intuitive variable to label the system. The average energy of the thermometer is microscopic and of order T . If C_V is negative, the thermometer energy distribution diverges. Its mean energy, controlled by the second order term, diverges, and the thermometer explodes. We call this second order divergence. Thus if the expansion does not converge, the parameter T becomes physically meaningless. Canonically the system has no temperature, and quantities defined in terms of derivatives with respect to temperature are meaningless.

So, for instance, negative heat capacity is, at the very least, a misnomer! The mathematically well defined but physically meaningless quantity $T = \left(\frac{\partial S}{\partial E}\right)^{-1}$ cannot be called temperature. In order to avoid deleterious confusion we suggest the name *Talitha* or *Tempura*, depending upon one's ethnic persuasion.

3.2.2 Second method

Let us recall the equation

$$\rho(E) = \frac{1}{2\pi i} \mathcal{Z}(\beta_0) \exp(\beta_0 E) \int \exp\left(-\frac{(\beta - \beta_0)^2}{2\sigma_\beta^2}\right) di\beta. \quad (40)$$

The saddle point located at $\beta = \beta_0 = \frac{1}{T}$ exists only if $\sigma_\beta^2 = \frac{1}{T^2 C_V}$ is positive. If C_V is negative the integrand diverges away from β_0 . Conceptually $\beta_0 = \frac{1}{T}$ is the least probable value of the distribution in β , hardly a meaningful choice to characterize the system. Again, if $C_V < 0$ the temperature remains undefined.

In conclusion: systems whose microcanonical entropy versus energy curve presents a negative slope $\frac{\partial S}{\partial E} < 0$ can be formally assigned a negative temperature in the canonical language as the most probable value of a peaked distribution with finite variance. However, when placed into contact with a thermometer, the average energy of the thermometer will diverge. This a first order divergence.

Systems for which $\frac{\partial^2 S}{\partial E^2}$ is positive (negative specific heat) cannot be assigned a meaningful temperature in the canonical language. The quantity $T = \left(\frac{\partial S}{\partial E}\right)^{-1}$ is the least probable value of the distribution. A thermometer in contact with such systems will be subject to a runaway increase in its mean energy. This a second order divergence.

4 Is equilibrium possible between anomalous and normal systems?

Let us consider two systems with the same $\frac{\partial S}{\partial E}$ in contact with each other. Can they be at equilibrium? Let their entropies and energies be S_1, S_2, E_1 and E_2 . Now let us transfer a small amount of energy ε from one to the other

$$S = S_1(E_1 + \varepsilon) + S_2(E_2 - \varepsilon). \quad (41)$$

The canonical expansion gives

$$S = S_1(E_1) + S_2(E_2) - \frac{\varepsilon}{T} + \frac{\varepsilon}{T} - \frac{1}{2} \frac{\varepsilon^2}{T^2} \left(\frac{1}{C_1} + \frac{1}{C_2} \right). \quad (42)$$

If both C_1 and C_2 are positive the system is stable. If $C_1 < 0$ and $C_2 < 0$ the system is unstable and there will be a runaway transfer of energy from one system to the other. If $C_1 > 0$ and $C_2 < 0$ the system is stable only if $C_1 + C_2 < 0$. Thus, the negative heat capacity must be bigger in absolute value than the positive heat capacity.

5 Signals of phase transitions in systems big and small

The advent of nano physics in material sciences on the one hand, and the realization that nuclear physics belongs to the same realm on the other, brings to fore the problem of connecting the properties of the infinite system to those of the mesoscopic system.

Recently, special attention has been paid to phase transitions in small systems and to their characterization. A variety of signals has been proposed to identify phase transitions in mesoscopic systems, of which the most celebrated are: a) “convex intruders” in the entropy S versus energy E diagram and the germane phenomena of negative heat capacities; b) Bimodality in the appearance of phases under the same set of conditions (e.g. temperature T , density ρ , pressure p , etc.), for instance either all liquid or all vapor but not both simultaneously; c) Fisher-like scaling plots of vapor clusters in equilibrium with either an infinite or mesoscopic liquid phase [5,3].

All of these signals have been studied numerically in certain models like Ising or Potts models with the hope that their appearance in physical experiments might be used for the identification of a phase transition and for its eventual characterization.

This brings forth the need for a critical analysis of these signals and their interpretation beyond the anecdotal nature of numerical simulations. This need is particularly acute for atomic nuclei where on one hand traditional experimental approaches are not accessible and, on the other hand, the presence of a long range force (Coulomb) raises disturbing questions even on the possibility of such systems presenting a thermodynamic phase transition. In what follows we shall analyze the signals of convex intruders and related negative heat capacities, as well as bimodality, making a special effort to retain a solid connection with thermodynamics.

5.1 Negative heat capacities without phase transitions

A convex intruder is defined as an energy value E in a micro-canonical model where (at constant volume V)

$$\left. \frac{\partial^2 S}{\partial E^2} \right|_V > 0 \quad (43)$$

where S is the entropy of the system in question. Since in standard thermodynamics

$$\left. \frac{\partial^2 S}{\partial E^2} \right|_V = -\frac{1}{T^2} \frac{1}{C_V} > 0 \quad (44)$$

it follows that the specific heat at constant volume $C_V < 0$, *granted of course that it makes sense to define the variables T and C_V as temperature and the specific heat in such an anomalous energy range.*

Down sloping caloric curves and negative heat capacities also seem to appear in canonical and grand canonical treatments of simple models.

It has been claimed that the appearance of a negative heat capacity ipso facto demonstrates the presence of a phase transition in a finite system. In this section we show:

1. negative heat capacities may appear in the infinite systems even in the absence of a phase transition and they are perfectly unsurprising;
2. negative heat capacities in finite systems undergoing phase transitions can be related to surface effects, can be simply described in terms of surface free energies, and being surface related, they depend on the vagaries of boundary conditions at times unwittingly introduced in the model under study.

First let us show how a negative heat capacity may appear in a single phase (vapor) of the infinite system.

Let us define

$$C_X = \frac{\delta Q}{\delta T}\Big|_X = T \left(\frac{\partial S}{\partial T}\Big|_p + \frac{\partial S}{\partial p}\Big|_T \frac{\partial p}{\partial T}\Big|_X \right) \quad (45)$$

where X stands for a particular direction in the pressure-temperature (p - T) plane. Since $\frac{\partial S}{\partial p}\Big|_T = -\frac{\partial V}{\partial T}\Big|_p$ we obtain

$$C_X = C_p - \frac{\partial V}{\partial T}\Big|_p T \frac{\partial p}{\partial T}\Big|_X. \quad (46)$$

For an ideal vapor $\frac{\partial V}{\partial T}\Big|_p = \frac{1}{p}$ and $\frac{T}{p} = V_m$ is the molar volume. Therefore $C_X = C_p - V_m \frac{\partial p}{\partial T}\Big|_X$. For sufficiently large V_m and for a steep enough trajectory on the p - T plane, C_X becomes negative even in an “ideal” gas! A well quoted example of this situation arises along the liquid-vapor coexistence curve where

$$\frac{dp}{dT} = \frac{\Delta H_m}{T \Delta V_m} \quad (47)$$

with ΔH_m as the molar enthalpy of evaporation. Here we have $C_X = C_p - \frac{\Delta H_m}{T}$ showing that for a saturated vapor at sufficiently small temperatures C_X becomes negative.

However, this has nothing to do with phase transitions since eq. (46) shows that negative heat capacities can occur for an ideal vapor as well!

A similar “strange phenomena” occurs for the thermal expansion coefficient

$$\frac{dV}{dT}\Big|_X = \frac{dV}{dT}\Big|_p + \frac{dV}{dp}\Big|_T \frac{dp}{dT}\Big|_X. \quad (48)$$

For an ideal vapor

$$\frac{dV}{dT}\Big|_X = \frac{1}{p} \left(1 - V_m \frac{dp}{dT}\Big|_m \right). \quad (49)$$

Again, there is a whole range of conditions for which

$$V_m \frac{dp}{dT}\Big|_m > 1 \quad (50)$$

and the thermal expansion coefficient is negative. For instance this can occur along coexistence, according to

$$\frac{dV}{dT}\Big|_C = \frac{1}{p} \left(1 - V_m \frac{\Delta H_m}{T} \right). \quad (51)$$

Again, this has nothing to do with phase transitions but just with the standard properties of an ideal gas.

5.2 More on convex intruders, temperature and heat capacities

In a microcanonical system, the natural variables are the entropy S , energy E , volume V and the particle number N . Occasionally an auxiliary variable

$$T^{-1} = \frac{\partial S}{\partial E}\Big|_{N,V} \quad (52)$$

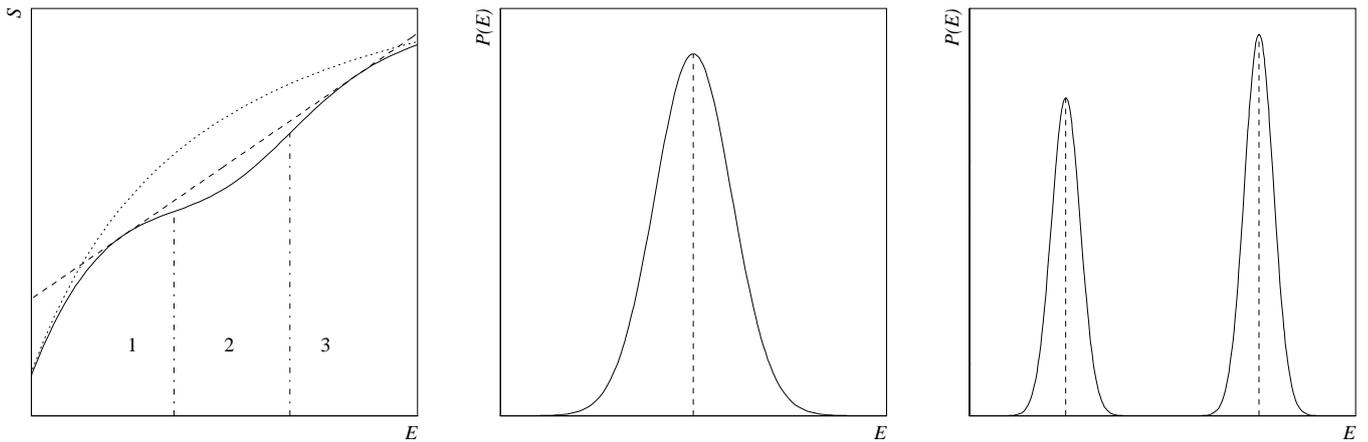


Fig. 1. Left: a plot of entropy S as a function of energy E . The dotted curve shows the usual $S(E)$ behavior. The solid curve shows the $S(E)$ behavior with a convex intruder. The dashed line shows the common tangent. The dash-dot lines show the inflection points. Middle: the probability distribution $P(E)$ for usual $S(E)$ behavior. Right: the probability distribution $P(E)$ for the $S(E)$ behavior with a convex intruder.

is introduced to make a connection with ordinary thermodynamical observations.

In a grand canonical system the natural variables are the free energy F , the temperature T and the chemical potential μ . Are the two temperatures equivalent?

In general they are not. In the former case assigning T is equivalent to assigning E . In the latter, T corresponds to an energy distribution

$$P(E) \sim e^{S(E) - \frac{E}{T}} \quad (53)$$

which derives physically from the “openness” of the canonical system and from its state of energy equilibrium with the environment.

However, if certain conditions are obtained, it is accurate to speak of the two temperatures interchangeably.

Let us consider a microcanonical system which admits a “convex intruder” in the function $S = S(E)$ as in Fig. 1. In regions 1 and 3 the function is concave and in region 2

convex. In regions 1 and 3 we can properly define a temperature according to Eq. (52) at any fixed energy E . The corresponding canonical temperature generates a distribution $P(E)$ according to Eq. (53) which looks like the middle plot of Fig. 1 provided that $\frac{\partial^2 S}{\partial E^2} < 0$. This distribution gives the most probable energy equal to the microcanonical energy E . In other words, if we place the microcanonical system with energy E (and auxiliary temperature T) in contact with a thermostat at temperature T one will observe the evolution of the microcanonical δ -function for E into a “gaussian.” Nothing much has happened.

In region 2, however, while we can always calculate a temperature according to Eq. (52) at a given energy E the corresponding canonical distribution of energy at that temperature exhibits the bimodal distribution shown in right most plot of Fig. 1. The two peaks correspond to the position of the common tangent point no matter what

T is. The ensemble splits into two sub-ensembles, which have very different energies, but a unique temperature (the common tangent temperature) $T_{\text{tang}} \neq T$ (except for a point). The area under the two peaks corresponds to a linear partition of the available energy. Notice that this guarantees the maximization of the total entropy which will ride not on the convex intruder, but on the common tangent. Consequently, the microcanonical “temperature” becomes physically meaningless as well as any quantity like heat capacity that is based upon such a temperature. In this case, while T and C_V can still be defined mathematically, they lose their physical meaning and their usefulness.

5.3 Negative heat capacities and first order phase transitions in nuclei

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.

Renewed attention to phase transitions has been generated by studies of models with either short range interactions (e.g. the lattice (Ising) gas model [6, 7]). Features expected to disappear in the thermodynamic limit were noticed and were claimed to be characteristic indicators of phase transitions in mesoscopic systems. For instance, first order phase transitions were associated with anomalous convex intruders in the entropy versus energy curves, resulting in back-bendings in the caloric curve, and in negative heat capacities. These anomalies have been at-

tributed to a variety of causes, the foremost of which are surface effects.

In the context of nuclear physics, microcanonical models of nuclear multifragmentation have associated the anomalies of a convex intruder with the onset of multifragmentation. Recently, the claim has been made of an empirical observation of these anomalies, such as negative heat capacities in nuclear systems. 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 section we investigate the subject of caloric curves and heat capacities of finite systems in the coexistence region and the underlying role of varying potential energies (“ground states”) with system size on the basis of simple and general thermodynamical concepts. Our study applies to leptodermous (thin skinned) van der Waals-like fluids and to models such as Ising, Potts, and lattice gas.

Let us consider a macroscopic drop of a van der Waals fluid with A constituents in equilibrium with its vapor. The vapor pressure p at temperature T is given by the Clapeyron equation

$$\frac{dp}{dT} = \frac{\Delta H_m}{T \Delta V_m} \quad (54)$$

where ΔH_m is the molar vaporization enthalpy and ΔV_m is the molar change in volume. It gives a direct connection between the “ground state” properties of the system and the saturation pressure along the coexistence line. In fact, we can write $\Delta H_m = \Delta E_m + P \Delta V_m \sim \Delta E_m + T$. For $T \ll \Delta E$, $\Delta H_m \approx a_v$ can be identified approxi-

mately with the liquid-drop volume coefficient in the absence of other terms like surface and Coulomb, etc. Assuming $\Delta V_m \approx V_m^{\text{vapor}}$, that the vapor is ideal and that ΔH_m is constant with T , Eq. (54) can be integrated giving

$$p \simeq p_o \exp\left(-\frac{\Delta H_m}{T}\right). \quad (55)$$

Equation (55) represents the p - T univariant line in the phase diagram of the system if ΔH_m is assigned its bulk value ΔH_m^0 . It was observed long ago that [4], for a drop of finite size, ΔH_m must be corrected for the surface energy of the drop

$$\Delta H_m = \Delta H_m^0 + \Delta H_m^s = \Delta H_m^0 - a_s \frac{2A^{2/3}}{3A} \quad (56)$$

where γ is the surface tension, S_m is the molar surface of the drop of radius r , and a_s is the surface energy coefficient. Substitution in Eq. (55) leads to

$$\begin{aligned} p &= p_o \exp\left(-\frac{\Delta H_m^0}{T} + \frac{2a_s}{3A^{1/3}T}\right) \\ &= p_{\text{bulk}} \exp\left(\frac{2a_s}{3A^{1/3}T}\right). \end{aligned} \quad (57)$$

At constant T the vapor pressure increases with decreasing size of the drop (see Fig. 2).

Let us now consider the case of isobaric evaporation of a drop starting from a drop with A_0 constituents and evaporating into a drop with $A < A_0$ constituents. Let us now define the drop size parameter $y = \frac{A_0 - A}{A_0}$. At constant pressure

$$p_o \exp\left(-\frac{\Delta H_m^0}{T}\right) = p_o \exp\left(-\frac{\Delta H_m(y)}{T_y}\right), \quad (58)$$

from which follows

$$\frac{T_y}{T_\infty} \simeq \frac{\Delta H_m(y)}{\Delta H_m^0} \simeq 1 - \frac{1}{A^{1/3}} \simeq 1 - \frac{1}{A_0^{1/3}(1-y)^{1/3}}. \quad (59)$$

Thus, a slight decrease in temperature is predicted as the drop evaporates isobarically, thus leading to a negative isobaric heat capacity in the coexistence region as illustrated in Fig. 2. As the drop is evaporating at constant pressure, the drop moves from one coexistence curve to another according to its decrease in radius, and thus to progressively lower temperatures. This slight effect is due not to an increase in surface as the drop evaporates, since the drop surface of course diminishes as $A^{2/3}$, but to the slight increase of molar surface which does increase as $A^{-1/3}$. Also, the formation of bubbles in the body of the drop is thermodynamically disfavored by the factor $f = \exp(-\gamma\Delta S/T)$ where ΔS is the surface of the bubble.

Let us now move to the amply studied cases of lattice gas, Ising, and Potts models. We consider first an evaporating finite system in three dimensions of size $A_0 = L^3$, with open boundary conditions. This case is essentially identical to the case of a drop discussed above (see Fig. 2). For maximal density at $T = 0$ (the ground state) $y = 0$ and the entire cubic lattice is filled. For decreasing densities, always at $T = 0$ a single cluster of minimum surface is present, which evolves from a cube to a sphere. The associated change in surface is shown in Fig. 2. The caloric curve from $y = 0$ to $y = 1/2$ is essentially flat like in the infinite system, and the heat capacity is trivially infinite.

The introduction of periodic boundary conditions rids the system of “dangling bonds,” as it were, by repeating a cubic lattice of side L periodically along the three coordinates. These conditions, lead to peculiar consequences.

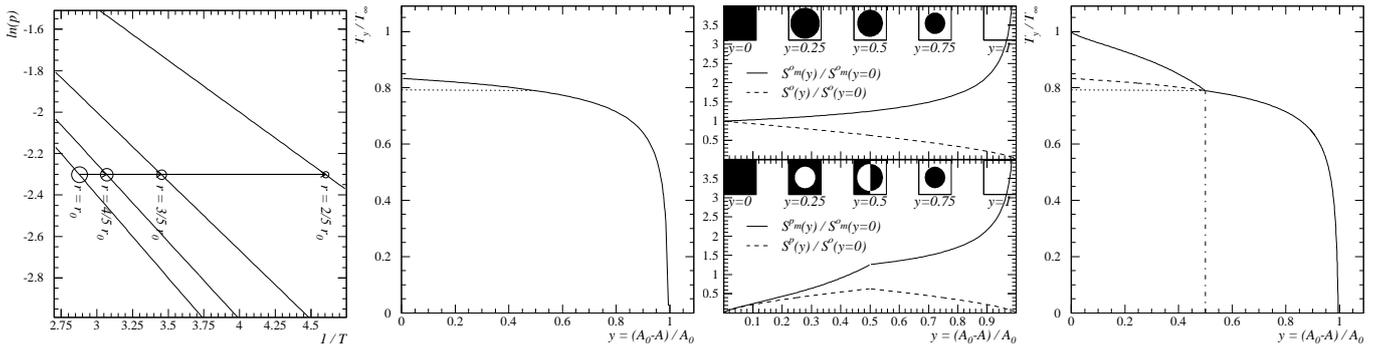


Fig. 2. First plot: the log of the saturated vapor pressure as a function of inverse temperature for different droplet radii. Open circle sizes are proportional to the droplet radius. Arrows illustrate the path of evaporation at constant pressure. Second plot: Temperature as a function of droplet size for a drop evaporating at constant pressure (open boundary conditions). The solid line shows the case of a spherical drop, while the dotted line shows the case of a finite cubic lattice evolving as in the top figure of the third plot. The surface S^o (dashed) and molar surface S_m^o (solid) area of a drop for open boundary conditions normalized to their values at $y = 0$. Third plot: Top (Bottom): The surface S^p (dashed) and molar surface S_m^p (solid) area of a drop for open (periodic) boundary conditions normalized to their values at $y = 0$. In-sets show the configurations at various values of y . Fourth plot: Temperature as a function of droplet size for a drop evaporating at constant pressure (periodic boundary conditions). The solid line shows the case of a finite cubic lattice evolving as in the bottom figure of the third plot, while the dotted line and the dashed line are the same as in second plot and the vertical dash-dotted line indicates the case of 50% occupation.

At $y = 0$, the lattice is filled with particles so that $\Delta H_m(0) = \Delta H_m^0$ characteristic of the infinite system. As y increases at fixed lattice size, a bubble develops in the cube and surface is rapidly created (see Fig. 2). The bubble develops since the periodic boundary conditions prevent evaporation from the surface. The bubble grows with increasing y until it touches the sides of the lattice. This occurs for $y \approx 1/2$. At nearly $y = 1/2$ and beyond, the “stable” configuration is a drop that eventually vanishes at $y = 1$. The change in surface associated with the range $0 \leq y \leq 1$ as well as the molar surface are shown in Fig. 2.

The evaporation enthalpy thus becomes

$$\Delta H_m(y) \simeq a_v \left(1 - \frac{y^{2/3}}{A_0^{1/3} (1-y)} \right) \quad (60)$$

from $y = 0$ to $y = 1/2$, and

$$\Delta H_m(y) \simeq a_v \left(1 - \frac{1}{A_0^{1/3} (1-y)^{1/3}} \right) \quad (61)$$

from $y = 1/2$ to $y = 1$. As a consequence, for periodic boundary conditions

$$\frac{T_y}{T_\infty} \simeq 1 - \frac{y^{2/3}}{A_0^{1/3} (1-y)} \quad (62)$$

from $y = 0$ to $y = 1/2$, while from $y = 1/2$ to $y = 1$ Eq. (59) holds.

The dramatic effect of periodic boundary conditions can be seen in Fig. 2. The temperature decreases substantially with increasing y , due to the fact that the molar enthalpy at $y = 0$ assumes its bulk value ΔH_m^0 and must meet the previous case of open boundary conditions for $y = 1/2$. This may well explain the calculated negative

heat capacities reported in literature, as due to the unnatural choice of boundary conditions.

5.4 Bimodality

Bimodality is offered as a signal of phase transitions in finite (and even infinite) systems. The history of bimodality traces back to the text book “Thermodynamics of small systems” [8], and refers to the fact that given for instance the chemical potential μ or p and T constant either one of the two phases is present and not both in arbitrary relative amounts such as in standard thermodynamics where all intermediate densities associated with arbitrary relative abundances of the phases are equiprobable.

The reason given for it is the interface created by the coexisting phases and the associated free energy cost which depresses any coexisting configuration by a factor of $\exp\left(-\frac{c\Delta s}{T}\right) \sim \exp\left(-\frac{kN^{2/3}}{T}\right)$; c is the surface, Δs is the surface created, k is the surface free energy coefficient and N is the particle number of the system with the surface.

An immediate criticism that can be raised against this proposition is the fact that it holds only if the pure phases do not have surfaces and surface energies of their own. In general this is not the case. Rather, surface is present at all times, and how it affects coexistence ends up depending on the configurations and vagaries of the boundary conditions, as well shall endeavor to show.

Let us analyze a case that comes closest to these expectations. This is offered to us by a calculations based on an Ising system [9]. The calculation is performed grand canonically (i.e. at constant μ, T) in a finite cell of given

size, with periodic boundary conditions. Above the critical temperature T_c the mean density has a single peak in the probability distribution P corresponding to the single fluid phase. Below T_c two well separated peaks in P appear, one corresponding to the vapor, the other to the liquid. Each realization is either all vapor like or all liquid like, while essentially no realization corresponds to the mixture of the two phases. This is called bimodality. The reason for this is the original explanation. The mixed phase involves the appearance of interfaces between the two phases with the associated free energy increase.

Convincing as this may be, this example works only because of the periodic boundary conditions. Since the calculation is performed grand canonically (i.e. μ is constant rather than the number of particles N), interface surfaces do not appear only if the vapor fills the cell and the rest of the universe generated by the periodic boundary conditions, or if the liquid fills the cell and the rest of the universe generated by the periodic boundary conditions at the same μ . The removal of periodic boundary conditions immediately creates a surface around the cell with the attendant surface free energy even if a single phase is present. In particular, since the surface free energy coefficient is larger for the case of the liquid-vacuum interface than for that of the vapor-vacuum interface, it follows that the bimodality disappears and only the vapor like phase will be manifested. This is all the more interesting because a liquid-like cell would readily compare with a hot nucleus, which would be then unstable at the same μ, T with respect to the vapor-like phase. Thus bimodality in nuclear

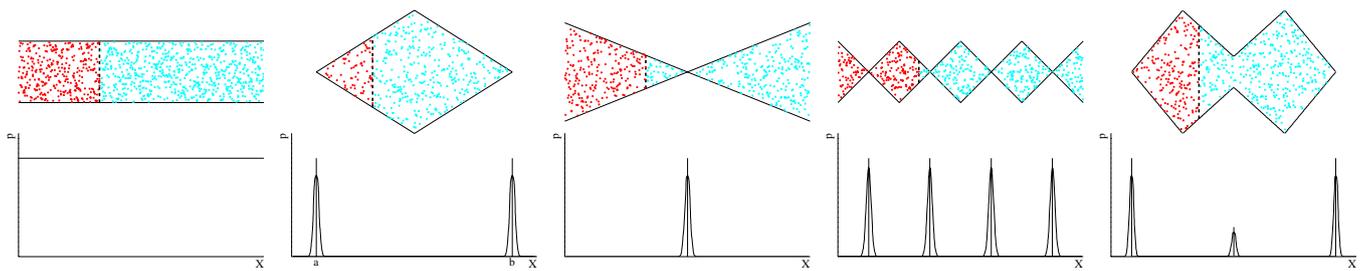


Fig. 3. From left to right: the first, second, third, fourth and fifth examples. Top plots show the configuration of the container and the phases. Bottom plots show (schematically) the probability distribution of the phases. See text for further details.

systems seems to be excluded by the very typical calculations that offer it as a signal of a phase transition.

A more realistic spherical geometry suggests a spherical liquid drop surrounded by its vapor also confined in a spherical shell extending into vacuum. Even in this case, which is a very realistic representation of a nucleus surrounded by its vapor, there can never be bimodality, since as before the liquid to vapor surface energy is much larger than the vapor to vacuum surface energy.

In order to appreciate the role of boundary conditions on the uni or bi modality, consider the following pedagogical examples all shown Fig. 3. In all examples we consider only the two phase interface to be active while we assume the phase-container interface to be inert. For simplicity the two phases are taken to have the same density.

Our first example is of an infinite cylinder of constant radius (a torus). The total free energy including surface is indifferent to the position of the interface. This is the classical case observed in thermodynamics where the equilibrium is indifferent with respect to X .

Our second example is of two cones connected by their bases. The free energy has a minimum at the apex of each cone (a and b). Thus we have perfect bimodality.

Our third example is of two cones connected by their vertices. The free energy has a minimum at the connection and the system portrays unimodality.

Our fourth example is of a sequence of cones connected alternately by their bases and vertices. The free energy has a maximum at each vertex connection and the system portrays n^{th} -modality.

Our fifth example shows the free energy has an absolute maximum at each end of the system and a local maximum in the middle. Thus the system portrays weak trimodality as shown in Fig. 3.

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