Failure of thermodynamics near a phase transition

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In the vicinity of a first-order phase transition, the equation of state might be different when the extensive variable is controlled instead of the intensive one, violating the uniqueness of thermodynamics. A sufficient condition for this nonequivalence to survive at the thermodynamical limit is worked out for classical systems. If energy consists of a kinetic and a potential part, the microcanonical ensemble does not converge towards the canonical ensemble when the kinetic heat capacity is larger than the modulus of the negative interaction heat capacity.

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Phase transitions are universal properties of matter in interaction. In macroscopic physics, they are anomalies in the system equation of state (EoS) and hence classified according to the degree of nonanalyticity of the EoS at the transition point. In this context, a phase transition appears as an intrinsic property of the system and not of the statistical ensemble used to describe the equilibrium. Indeed, all the possible statistical ensembles are supposed to converge toward the same EoS and the various thermodynamical potentials are supposed to be related by simple Legendre transformations leading to a unique thermodynamics. In most textbooks the equivalence between the different statistical ensembles is demonstrated at the thermodynamical limit through the Van Hove theorem [1]. On the other side for finite systems, it is known that two ensembles that put different constraints on the fluctuations of the order parameter lead to qualitatively different EoS close to a first-order phase transition. As an example, when the variation of order parameter produces a change in the system energy, the microcanonical (at fixed energy) heat capacity diverges to become negative while the canonical (at fixed temperature) one remains always positive and finite [2,3]. This major discrepancy can be of primordial importance for mesoscopic systems undergoing a phase transition as now studied in many fields of physics from Bose condensates to the quark-gluon plasma. Moreover, such inequivalences may survive at the thermodynamical limit for systems involving long-range forces such as self-gravitating objects [4,5]. Looking at the general properties of the order parameter distribution a sufficient condition for this behavior to show up will be explicitly worked out.

Let us first concentrate on finite systems. For simplicity we will consider the microcanonical and the canonical ensemble characterized by the energy E and the temperature β^{-1} respectively, but our discussion is valid for any couple of conjugated extensive and intensive variables.

The microcanonical ensemble is characterized by the level density $W(E)$ and the entropy $S=\ln W$. The caloric curve is then $T^{-1}=\partial_E S$. The canonical partition sum is the Laplace transform of W: $Z_\beta=\int W(E)\exp(-\beta E)dE$. In this article, we will assume that the partition sum converges; this is not always the case as discussed in Ref. [6] and indeed the impossibility to normalize the distribution $W\exp(-\beta E)$ is already a known case of ensemble inequivalence.

In finite systems, the canonical ensemble differs from the microcanonical one since it does not correspond to a unique energy but to a distribution $P_\beta(E)=\exp[S(E)-\beta E-\ln Z_\beta]$. If P_β has a single maximum the average energy $\langle E\rangle_\beta=-\partial_\beta \ln Z_\beta$ can also be computed from the distribution P_β. Using a saddle point approximation around the most probable energy $\overline{E}_\beta$ we get

$$\langle E\rangle_\beta=\int dE\,E\,e^{-(E-\overline{E}_\beta)^2/2C}g_\beta(E-\overline{E}) \tag{1}$$

with $g_\beta(x)=c_0+c_3x^3+c_4x^4+\dots$. If P_β is symmetric, $\langle E\rangle_\beta=\overline{E}_\beta$. The definition of saddle implies

$$T^{-1}\equiv\partial_E S(\overline{E}_\beta)=\beta \tag{2}$$

meaning that the microcanonical caloric curve $T(\overline{E})$ exactly coincides with the canonical one $\beta^{-1}(\langle E\rangle)$. However, in a finite system the distribution may not be symmetric so that the two curves can be shifted : $\langle E\rangle_\beta=\overline{E}_\beta+\delta_\beta$, where $\delta_\beta=\int dx\,x\exp(-x^2/2C)\tilde{g}_\beta(x)=3c_3\sqrt{2\pi C^5}+\dots$ with $\tilde{g}_\beta$ the series of the odd terms of g_β. However, the shift δ is in most cases small so that when P_β has a unique maximum the ensembles are almost equivalent even for a finite system.

A more interesting situation occurs in first-order phase transitions where P_β has a characteristic bimodal shape [7–9] with two maxima $\overline{E}_\beta^{(1)}$, $\overline{E}_\beta^{(2)}$ that can be associated with the two phases and a minimum $\overline{E}^{(0)}$. These three solutions of Eq. (2) imply a backbending for the microcanonical caloric curve. A single saddle point approximation is not valid in this case; however, it is always possible to write $P_\beta=m_\beta^{(1)}P_\beta^{(1)}+m_\beta^{(2)}P_\beta^{(2)}$ with $P_\beta^{(i)}$ monomodal normalized probability distribution peaked at $\overline{E}_\beta^{(i)}$. The canonical mean energy is then the weighted average of the two energies

$$\langle E\rangle_\beta=\tilde{m}_\beta^{(1)}\overline{E}_\beta^{(1)}+\tilde{m}_\beta^{(2)}\overline{E}_\beta^{(2)} \tag{3}$$

with $\tilde{m}_\beta^{(i)}=m_\beta^{(i)}\int dE\,P_\beta^{(i)}(E)E/\overline{E}_\beta^{(i)}\simeq m_\beta^{(i)}$, the last equality holding for symmetric distributions $P_\beta^{(i)}$. Since only one mean energy is associated with a given temperature β^{-1}, the canonical caloric curve is monotonic, meaning that in the first-order phase transition region the two ensembles are not equivalent.

If instead of looking at the average $\langle E\rangle_\beta$ we look at the most probable energy $\overline{E}_\beta$, this (unusual) canonical caloric curve is identical to the microcanonical one [see Eq. (2)] up to the transition temperature β_t^{-1} for which the two components of $P_\beta(E)$ have the same height. At this point the most probable energy jumps from the low- to the high-energy branch of the microcanonical caloric curve. The most probable canonical energy is still a monotonic curve but it presents a plateau at β_t^{-1} which is equivalent to the Maxwell construction since

$$S(\overline{E}_\beta^{(2)})-S(\overline{E}_\beta^{(1)})=\int_{\overline{E}_\beta^{(1)}}^{\overline{E}_\beta^{(2)}}\frac{dE}{T}=\beta(\overline{E}_\beta^{(2)}-\overline{E}_\beta^{(1)}). \qquad (4)$$

Therefore, the difference between the canonical and microcanonical caloric curves remains when one is looking at the most probable energy instead of the average.

The question arises whether this violation of ensemble equivalence survives towards the thermodynamical limit. This limit can be expressed as the fact that the thermodynamical potentials per particle converge when the number of particles N goes to infinity: $f_{N,\beta}=\beta^{-1}\ln Z_\beta/N\to\overline{f}_\beta$ and $s_N(e)=S(E)/N\to\overline{s}(e)$ where $e=E/N$. Let us also introduce the reduced probability $p_{N,\beta}(e)=[P_\beta(N,E)]^{1/N}$ which then converges towards an asymptotic distribution $p_{N,\beta}(e)\to\overline{p}_\beta(e)$ where $\overline{p}_\beta(e)=\exp[\overline{s}(e)-\beta e+\overline{f}_\beta]$. Since $P_\beta(N,E)\approx[\overline{p}_\beta(e))^N$ one can see that when $\overline{p}_\beta(e)$ is normal the relative energy fluctuation in $P_\beta(N,E)$ is suppressed by a factor $1/\sqrt{N}$. At the thermodynamical limit P_β reduces to a δ-function and the ensemble equivalence is recovered. To analyze the thermodynamical limit of a first-order phase transition [bimodal $p_{N,\beta}(e)$], let us introduce as before $\beta_{N,t}^{-1}$ the temperature for which the two maxima of $p_{N,\beta}(e)$ have the same height. For a first-order phase transition $\beta_{N,t}^{-1}$ converges to a fixed point $\overline{\beta}_t^{-1}$ as well as the two maximum energies $e_{N,\beta}^{(i)}\to\overline{e}_\beta^{(i)}$. For all temperatures lower (higher) than $\overline{\beta}_t^{-1}$ only the low (high) energy peak will survive at the thermodynamical limit since the difference of the two maximum probabilities will be raised to the power N. Therefore, below $\overline{e}_\beta^{(1)}$ and above $\overline{e}_\beta^{(2)}$ the canonical caloric curve coincides with the microcanonical one in the thermodynamical limit. In the canonical ensemble the temperature $\overline{\beta}_t^{-1}$ corresponds to a discontinuity in the state energy irrespectively of the behavior of the entropy between $\overline{e}_\beta^{(1)}$ and $\overline{e}_\beta^{(2)}$.

The microcanonical caloric curve in the phase transition region may either converge towards the Maxwell construction or keep a backbending behavior, since a negative heat capacity system can be thermodynamically stable even in the thermodynamical limit if it is isolated [10]. This point has been recently made in somewhat different words by Leyvraz and Ruffo [11]. Examples of a backbending behavior at the thermodynamical limit have been reported for a model many-body interaction taken as a functional of the hypergeometric radius in Ref. [4] and for the long-range Ising model [5]. This can be understood as a general effect of long-range interactions for which the topological anomaly leading to the convex intruder in the entropy is not cured by increasing the number of particles [5,12]. Conversely, for short-range interactions [3] the backbending is a surface effect which should disappear at the thermodynamical limit. This is the case for the microcanonical model of fragmentation of atomic clusters [13] and for the lattice gas model with fluctuating volume [14] . The interphase surface entropy goes to zero as $N\to\infty$ in these models leading to a linear increase of the entropy in agreement with the canonical predictions. From these examples, we can conclude that in the coexistence region the microcanonical equation of states may remain different from the canonical one even at the thermodynamical limit if the involved phenomena are not reduced to short-range effects.

Even if many different examples have been reported in the literature, the general conditions for ensemble inequivalence to show up stay up to now rather mysterious.

Within our approach based on the topology of the probability distribution of observables [9] we have just shown that ensemble inequivalence arises from fluctuations of the order parameter. Ensembles putting different constraints on the fluctuations of the order parameter lead to a different thermodynamics. In the case of phase transitions with a finite latent heat, the total energy usually plays the role of an order parameter except in the microcanonical ensemble which, therefore, is expected to present a different thermodynamics than the other ensembles. This inequivalence may remain at the thermodynamical limit depending upon the specific properties of the considered system. In particular, it may happen that the energy of a subsystem becomes an order parameter when the total energy is constrained by a conservation law or a microcanonical sorting. This frequently occurs for Hamiltonians containing a kinetic energy contribution: if the kinetic heat capacity is large enough we will now show that the kinetic energy becomes an order parameter in the microcanonical ensemble. This is almost a paradox since in any ensemble in which no energy conservation is imposed the kinetic energy has a trivial perfect gas behavior, while in the microcanonical ensemble it becomes an order parameter with the specific bimodal structure at the phase transition. Then, the microcanonical caloric curve presents at the thermodynamical limit a temperature jump in complete disagreement with the canonical ensemble.

Let us consider a finite system for which the Hamiltonian can be separated into two components $E=E_1+E_2$, that are statistically independent [$W(E_1,E_2)=W_1(E_1)W_2(E_2)$] and such that the associated degrees of freedom scale in the same way with the number of particles; we will also consider the case where $S_1=\ln W_1$ has no anomaly while $S_2=\ln W_2$ presents a convex intruder that is preserved at the thermodynamical limit. Typical examples of E_1 are given by the kinetic energy for a classical system with velocity independent interactions or other similar one-body operators [5].

The probability of getting a partial energy E_1 when the total energy is E is given by

$$P_E(E_1)=\exp[S_1(E_1)+S_2(E-E_1)-S(E)]. \qquad (5)$$

The extremum of $P_E(E_1)$ is obtained for the partitioning of the total energy E between the kinetic and potential components that equalizes the two partial temperatures $\overline{T_1}^{-1}=\partial_{E_1}S_1(\overline{E_1})=\partial_{E_2}S_2(E-\overline{E_1})=\overline{T_2}^{-1}$. If $\overline{E_1}$ is unique, $P_E(E_1)$ is monomodal and we can use a saddle point approximation around this solution to compute the entropy $S(E)=\ln\int_{-\infty}^{E}dE_1\exp[S_1(E_1)+S_2(E-E_1)]$. At the lowest order, the entropy is simply additive so that the microcanonical temperature of the global system $\partial_E S(E)=\overline{T}^{-1}$ is the one of the most probable energy partition. Therefore, the most probable partial energy $\overline{E_1}$ acts as a microcanonical thermometer. If $\overline{E_1}$ is always unique, the kinetic thermometer in the backbending region will follow the whole decrease of temperature as the total energy increases. Therefore, the total caloric curve will present the same anomaly as the potential one.

If conversely, the partial energy distribution is double humped [15], then the equality of the partial temperatures admits three solutions, one of them $\overline{E}_1^{(0)}$ being a minimum. At this point the partial heat capacities $C_1^{-1}=-\overline{T}^2\partial_{E_1}^2S_1(\overline{E}_1^{(0)})$ and $C_2^{-1}=-\overline{T}^2\partial_{E_2}^2S_2(E-\overline{E}_1^{(0)})$ fulfill the relation

$$C_1^{-1}+C_2^{-1}<0. \qquad (6)$$

This happens when the potential heat capacity is negative and the kinetic energy is large enough ($C_1>-C_2$) to act as an approximate heat bath: the partial energy distribution $P_E(E_1)$ in the microcanonical ensemble is then bimodal as the total energy distribution $P_\beta(E)$ in the canonical ensemble implying that the kinetic energy is the order parameter of the transition in the microcanonical ensemble. In this case the microcanonical temperature is given by a weighted average of the two estimations from the two maxima of the kinetic energy distribution

$$T=\partial_E S(E)=\frac{\overline{P}^{(1)}\sigma^{(1)}/\overline{T}^{(1)}+\overline{P}^{(2)}\sigma^{(2)}/\overline{T}^{(2)}}{\overline{P}^{(1)}\sigma^{(1)}+\overline{P}^{(2)}\sigma^{(2)}}, \qquad (7)$$

where $\overline{T}^{(i)}=T_1(\overline{E}_1^{(i)})$ are the kinetic temperatures calculated at the two maxima, $\overline{P}^{(i)}=P_E(\overline{E}_1^{(i)})$ are the probabilities of the two peaks and $\sigma^{(i)}$ their widths. At the thermodynamical limit Eq. (6) reads $c_1^{-1}+c_2^{-1}<0$, with $c=\lim_{N\to\infty}C/N$. If this condition is fulfilled the probability distribution $P_\beta(E)$ presents two maxima for all finite sizes and only the highest peak survives at $N=\infty$. Let E_t be the energy at which $P_{E_t}(\overline{E^{(1)}})=P_{E_t}(\overline{E^{(2)}})$. Because of Eq. (7) at the thermodynamical limit the caloric curve will follow the high (low) energy maximum of $P_E(E_1)$ for all energies below (above) E_t; there will be a temperature jump at the transition energy E_t.

Let us illustrate the above results with two examples for a classical gas of interacting particles. For the kinetic energy contribution we have $S_1(E)=c_1\ln(E/N)^N$ with a constant kinetic heat capacity per particle $c_1=3/2$. For the potential part

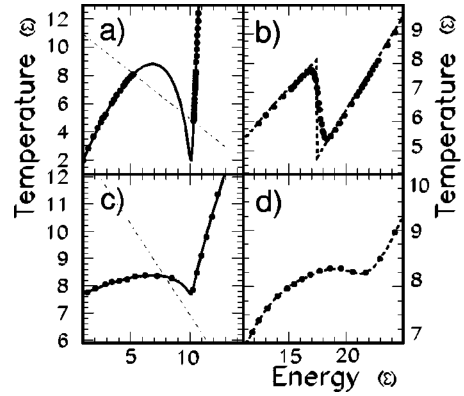

FIG. 1. Left panels: temperature as a function of the potential energy E_2 (full lines) and of the kinetic energy $E-E_2$ (dot-dashed lines) for two model equation of states of classical systems showing a first-order phase transition. Symbols: temperatures extracted from the most probable kinetic energy thermometer from Eq. (5). Right panels: total caloric curves (symbols) corresponding to the left panels and thermodynamical limit of Eq. (7) (dashed lines).

we will take two polynomial parametrizations of the interaction caloric curve presenting a backbending, which are displayed in the left part of Fig. 1 in units of an arbitrary scale ϵ. If the decrease of the partial temperature $T_2(E_2)$ is steeper than $-2/3$ [Fig. 1(a)] [4] Eq. (6) is verified and the kinetic caloric curve $T_1(E-E_1)$ (dot-dashed line) crosses the potential one $T_2(E_2)$ (full line) in three different points for all values of the total energy lying inside the region of coexistence of two kinetic energy maxima. The resulting caloric curve for the whole system is shown in Fig. 1(b) (symbols) together with the thermodynamical limit (lines) evaluated from the double saddle point approximation (7). In this case one observes a temperature jump at the transition energy. If the temperature decrease is smoother [Fig. 1(c)] the shape of the interaction caloric curve is preserved at the thermodynamical limit [Fig. 1(d)].

The occurrence of a temperature jump in the thermodynamical limit is easily spotted by looking at the bidimensional canonical event distribution $P_\beta(E_1,E_2)$ in the partial energies plane. This canonical probability is nothing but the product of the independent kinetic and potential canonical probabilities as shown in the left part of Fig. 2 for the two model equation of states of Fig. 1 at the transition temperature $\beta=\beta_t$. In the canonical ensemble the potential energy, as well as the total energy, plays the role of an order parameter while the kinetic energy distribution is normal. In order to discuss the microcanonical ensemble one has to introduce the total energy $E=E_1+E_2$. Keeping E and E_1 as variables instead of (E_1,E_2) is nothing but a simple coordinate change with unit Jacobian. Thus we can look at the canonical distribution as a function of E and E_1, $P_\beta(E,E_1)\propto\exp S_1(E_1)\exp S_2(E-E_1)\exp(-\beta E)$ which is shown in the right part of Fig. 2. The deformation of the event distribution induced by the microcanonical constraint does not cause a topological difference between our two model cases; this explains why both converge to the Maxwell construction for $N\to\infty$ in the canonical ensemble. If we now study the microcanonical ensemble we have to look at constant energy

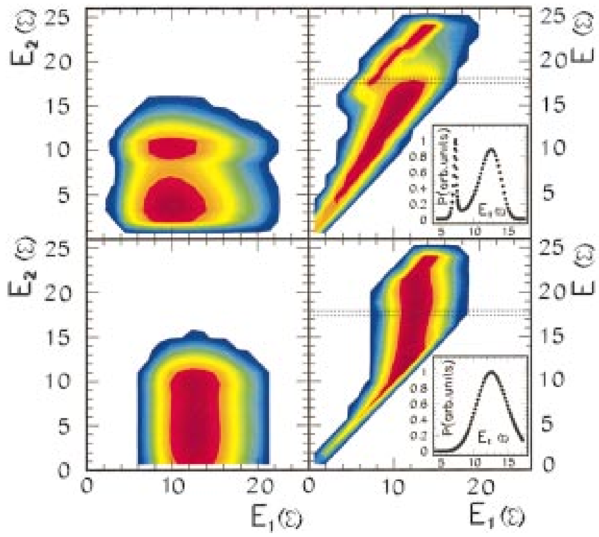

FIG. 2. (Color) Canonical event distributions in the potential versus kinetic energy plane (left panels) and total versus kinetic energy plane (right panels) at the transition temperature for the two model equations of state of Fig. 1. The insets show two constant total energy cuts of the distributions.

cuts of $P_\beta(E,E_1)$ leading to the microcanonical distribution $P_E(E_1)$ within a normalization constant. If the anomaly in the potential equation of state is sufficiently important, the distortion of events is such that one can still see the two phases coexist even after a sorting in energy as shown in the same Fig. 2 for two cuts of $P_\beta(E,E_1)$ at an energy close to the transition energy.

In conclusion, in this paper we have analyzed the thermodynamics of finite and infinite systems undergoing a first-order phase transition using two statistical ensembles. In the extensive (e.g., microcanonical) ensemble the events are sorted according to an observable quantity, the extensive variable, (e.g., energy) related to the order parameter while in the intensive (e.g., canonical) ensemble only the average value of the observable is constrained by means of a Lagrange parameter (e.g., the temperature). In such a physical situation the two statistical ensembles are not in general equivalent. For a finite system in the canonical ensemble, the energy has an average value that varies smoothly while the most probable energy makes a jump when the heat bath temperature varies. In the microcanonical ensemble the microcanonical temperature presents a backbending. In infinite systems, this nonequivalence between statistical ensembles may remain. We have shown that a generic behavior of the extensive ensemble can be a discontinuity in the associated intensive variable. In particular, microcanonical caloric curves present a sudden temperature fall at the transition energy if the negative heat capacity is sufficiently small in absolute value for the kinetic energy to play the role of a heat bath. In such a case the kinetic energy appears as a general order parameter specific of the microcanonical ensemble. Then the characteristics of the phase transition appear to be not only a system property but also depends upon the variable kept constant to define the considered equilibrium. This affects both finite systems under any interaction and infinite system with long-range forces. From the experimental point of view, contrary to the physical intuition based on macrosystems, the equations of state are expected to explicitly depend on the characteristic state variables of the considered ensemble of events, i.e., both the conserved quantities imposed by the dynamics and the sorting variables used in the data analysis. This implies the impossibility to define a unique thermodynamics, i.e., a unique EoS, for systems undergoing a first-order phase transition.

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