

Novel concepts for the systematic statistical analysis of phase transitions in finite systems

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Abstract. We review recent developments in the conceptual approach to a consistent systematic understanding of cooperative thermodynamic activity. The microcanonical statistical analysis is a powerful tool that is particularly useful for the investigation of analogs of phase transitions in finite systems, but it applies also in the extrapolation toward the thermodynamic limit. Whereas Maxwell construction in the coexistence region in the inverse caloric temperature space is a reasonable method for individual first-order-like transitions that are well-separated from other energetic regions of thermal activity, microcanonical inflection-point analysis is a systematic method that enables both the identification and classification of transitions of first and higher orders.

1. Introduction

Since the earliest observations that any physical system can exist in different thermodynamic phases, there has been a substantial interest in understanding the reasons for the qualitative changes that a macroscopic system is capable to experience while passing a transition point in the space of environmental parameters [1]. Conventional thermodynamics cannot explain the large-scale fluctuations and correlations that accompany a phase transition, but provides the basis for an adequate description that culminated in Ehrenfest's classification of phase transitions by locating discontinuities and divergences in thermodynamic variables (e.g., entropy, volume) and response quantities (specific heat, susceptibility, etc.), respectively. These quantities can be represented by distinct derivatives of appropriate thermodynamic potentials. For example, for a closed system of particles at constant temperature, pressure, and particle number, the thermodynamic potential is the Gibbs enthalpy $G(T, p, N)$. If we generally denote any thermodynamic potential that represents the thermodynamic system by $P(\mathbf{A})$, where \mathbf{A} is the vector of independent external thermodynamic variables (such as T , p , and N in the example above), then a phase transition is observed at a point \mathbf{A}_0 , if any of the derivatives of P with respect to any component of \mathbf{A} ,

$$\left(\frac{\partial^{(n)} P}{\partial A_i^{(n)}} \right)_{\mathbf{A}_0} \quad (1)$$

is discontinuous or divergent at \mathbf{A}_0 . The order of the transition is given by the lowest derivative n_0 that exhibits catastrophic behavior at the transition point. In most cases, only transitions of first ($n_0 = 1$) and second order ($n_0 = 2$) are distinguished. Each of the derivatives in Eq. (1)



can be understood as a response quantity. In our example, the response of G to a change of temperature is the entropy, $S(T, p, N) = -(\partial G/\partial T)_{p,N}$, and a discontinuity at a temperature T_0 signals a first-order phase transition. The second derivative of G with respect to T is related to the heat capacity at constant pressure, $C_p(T, p, N) = T(\partial S/\partial T)_{p,N} = -T(\partial^2 G/\partial T^2)_{p,N}$, which quantifies the response of the entropy to a change in temperature. A discontinuity or divergence of C_p at a critical temperature T_c indicates a second-order phase transition, provided the entropy is continuous at the transition point. Similar relations hold for responses to changes in the other natural thermodynamic variables of G .

However, Ehrenfest's theorem applies only in the thermodynamic limit, i.e., for very large systems, because thermodynamic quantities that describe the macrostate of finite systems do not exhibit any discontinuities or divergences. The interest in the understanding of thermodynamic activity in small or at least finite systems – with its extreme variant cooperativity – has rapidly grown recently. The sizes of nanotechnological applications and biological systems are microscopic or mesoscopic, i.e., surface effects affect the system's behavior to such an extent that the hypothetical extrapolation toward the thermodynamic limit is not helpful for the analysis of transitions in these systems. Therefore Ehrenfest's idea needs to be generalized.

The currently most promising approach is the so-called microcanonical analysis. Initially limited to first-order-like transitions by employing Maxwell's construction, the theory has recently been generalized in a systematic way that does not only allow for a unique identification of the transitions; it also enables the classification of the transitions similar to Ehrenfest's approach for large systems. This idea is based on the analysis of inflection points of the inverse microcanonical temperature.

In the following, we review the original idea of Maxwell's construction in the thermodynamic limit, its microcanonical version [1–10], and finally we discuss the basic features of the microcanonical inflection-point analysis [1, 11, 12].

2. Maxwell construction in thermodynamics

Transitions with phase coexistence, typically referred to as first-order phase transitions, are traditionally analyzed by means of Maxwell's construction. This method is necessary to remove the unphysical backbending branch that occurs for real gases described by the van der Waals equation in the pressure (p) versus volume (V) phase diagram for isotherms below the critical temperature T_{crit} . Since $(\partial p/\partial V)_{T < T_{\text{crit}}} > 0$ in this region, the compressibility is negative in the transition regime. The consequence would be a catastrophic instability of matter, although it is supposed to be in an equilibrium state. This is unphysical behavior and needs to be corrected. Figure 1(a) shows three van der Waals isotherms at temperatures above, at, and below the critical temperature.

It can be shown that in the thermodynamic limit the Gibbs free energies of the two coexisting phases (liquid, gas) must be identical for each macrostate in the transition region, $G_{\text{lg}} = G_{\text{l}} = G_{\text{g}}$. The unphysical behavior of the van der Waals equation can only be avoided if the pressure in the transition region remains constant. The value of this pressure, p_{lg} , is determined by the following consideration. Along the isotherm ($dT = 0$), $dG = V dp$. Hence, if the Gibbs free energies in both phases would not be identical, the gradient ($V = (\partial G/\partial p)_T$) would spontaneously drive the system into one of the phases. This does not occur in a real gas-liquid mixture. The stable equilibrium liquid-gas phase coexistence can be observed. Additional work, as can be expressed by the change of free energy $dF = -pdV$, is necessary to change the macrostate (actually only V , because p and T are constant) within the transition region. Therefore, the total transition free energy released in the evaporation process is given by

$$F_{\text{lg}} \equiv - \int_{V_{\text{l}}}^{V_{\text{g}}} p(V) dV = -p_{\text{lg}}(V_{\text{g}} - V_{\text{l}}). \quad (2)$$

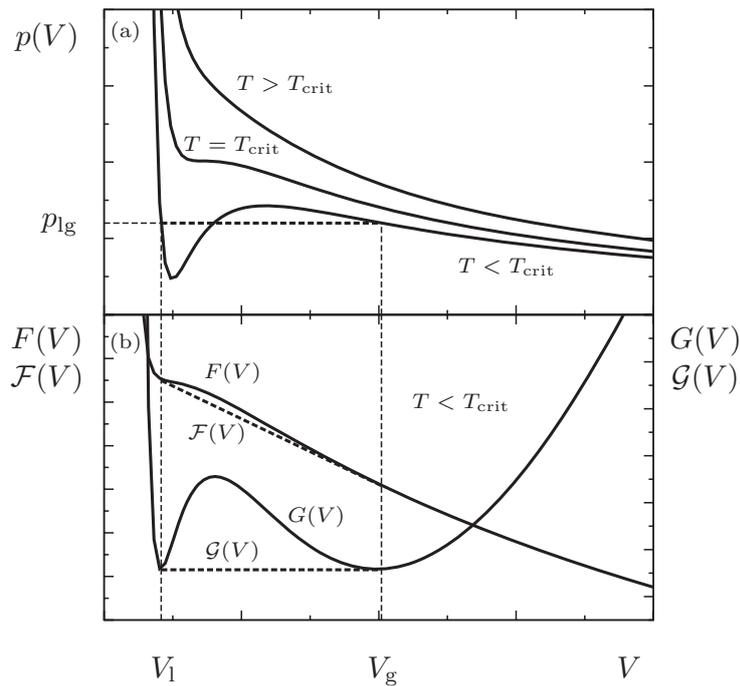


Figure 1. (a) Isotherms of the van der Waals gas $p(V)$ for temperatures T below, at, and above the critical temperature T_{crit} , and Maxwell line at $p = p_{\text{lg}}$. (b) Free energy $F(V)$, Gibbs construction for the free energy $\mathcal{F}(V)$ and Gibbs free energy $G(V)$ and its Gibbs hull $\mathcal{G}(V)$ at pressure $p = p_{\text{lg}}$ for the isotherm in (a) at $T < T_{\text{crit}}$.

where V_l and V_g denote the volumes at the respective phase boundaries, satisfying

$$\left(\frac{\partial F}{\partial V}\right)_{V_l} = \left(\frac{\partial F}{\partial V}\right)_{V_g} = -p_{\text{lg}} = \text{const} \quad (3)$$

in the interval $V \in [V_l, V_g]$. The area under the original curve $p(V)$ in this volume interval and the area bounded by p_{lg} are identical. The free energy as a function of the volume, $F(V)$, is shown in Fig. 1(b). Note the concavity $0 > (\partial^2 F / \partial V^2)_{T < T_{\text{crit}}} = -(\partial p / \partial V)_{T < T_{\text{crit}}} = 1/V\kappa$ of this function in the transition interval. Since neither V nor the compressibility κ can be negative, this behavior of F is unphysical.

The Maxwell construction for the subcritical isotherm corresponds to a Gibbs construction for the free energy: $\mathcal{F}(V) = F(V_l) - p_{\text{lg}}(V - V_l) \forall V \in [V_l, V_g]$, i.e., the slope of this double tangent of $F(V)$ is $-p_{\text{lg}}$. Since $\mathcal{F}(V) < F(V) \forall V \in [V_l, V_g]$, the macrostates $(p_{\text{lg}}, V_{\text{lg}} \in [V_l, V_g], T_{\text{lg}} < T_{\text{crit}})$ then indeed represent the stable and physical equilibrium states in the liquid-gas transition region. The hull of the Gibbs free energy, $\mathcal{G}(V) = \mathcal{F}(V) + p_{\text{lg}}V$, is constant and minimal in the coexistence regime, as required. Thus, it replaces $G(V) = F(V) + p_{\text{lg}}V$ as the appropriate thermodynamic potential for the van der Waals gas in the first-order transition region [see Fig. 1(b)]. As we have seen, the Maxwell construction is necessary for a physically consistent thermodynamic description of this model. It shall be noted that the problem lies in the equation of state. A statistical mechanics analysis of a microscopic model would not require to use Maxwell's construction method to "repair" unphysical behavior; the Maxwell line would establish itself in the thermodynamic limit.

3. Microcanonical analysis by Maxwell construction for first-order-like transitions in finite systems

For the statistical analysis of finite systems that experience transitions that exhibit clear signatures of a first-order transition, a Maxwell construction can be rewarding, although it is not required for thermodynamic consistency.

The most fundamental statistical property and the fingerprint of any given physical system is the microcanonical entropy $S(E) = k_B \ln g(E)$, where $g(E)$ is the density of the states of the system. Typically, $S(E)$ is a concave function, except in a region of the energetic space, in which the number of energetic microstates is suppressed to such an extent that the entropy curve loses its concave monotony and becomes convex. Since in this depletion region the entropy has an energetic width $\Delta Q > 0$ and connects energetic spaces which are associated with different phases of reduced thermodynamic activity, the extended region in-between accommodates macrostates, in which both phases coexist. It is therefore common to interpret ΔQ as the latent heat and to associate the entropic suppression in this region with a first-order transition, in analogy to thermodynamic first-order phase transitions in the thermodynamic limit.

Figure 2(a) shows a typical example for an entropic curve with a convex region. The depletion zone is bounded by the limiting energies of the ordered phase, E_o , and the disordered phase, E_d . The width of the entropic depletion zone is $\Delta Q = E_d - E_o$. Also shown is the double-tangent (Gibbs hull), which corresponds to a Maxwell construction in the (inverse) temperature curve $\beta(E) = 1/T(E)$, as plotted in Figure 2(b). It enables the definition of a unique transition temperature β_{tr} . The unique identification of transition points is a notorious problem in conventional, typically canonical, analyses for finite systems [13]. The boundaries E_o and E_d are defined by the points, where the Gibbs hull

$$\mathcal{H}(E) = S(E_o) + \beta_{tr}(E - E_o) = S(E_d) + \beta_{tr}(E - E_d) \quad (4)$$

touches $S(E)$: $\mathcal{H}(E_{o,d}) = S(E_{o,d})$. The total entropy change during the transition $\Delta S_{tr} = S(E_d) - S(E_o) = \mathcal{H}(E_d) - \mathcal{H}(E_o)$ can then be expressed in two ways:

$$\Delta S_{tr} = \int_{E_o}^{E_d} dE \beta(E) = \beta_{tr}(E_d - E_o). \quad (5)$$

As Fig. 2(b) also shows, the β curve resembles a third-order polynomial with a “backbending” region. For that reason, the Maxwell line β_{tr} possesses a third intersection point with $\beta(E)$, denoted by E_{tr} . It can be considered as the separation point, where the entropic weight of each of the both phases in the coexistence region is identical. In this formalism, it defines the transition state. The total entropy change in the order-dominated coexistence regime is

$$\Delta S_o = \int_{E_o}^{E_{tr}} dE \beta(E) = S(E_{tr}) - S(E_o) = \beta_{tr}(E_{tr} - E_o) - s_o \quad (6)$$

and for the disordered part

$$\Delta S_d = \int_{E_{tr}}^{E_d} dE \beta(E) = S(E_d) - S(E_{tr}) = \beta_{tr}(E_d - E_{tr}) + s_d, \quad (7)$$

where the right-hand side expressions are simply obtained by adding the areas according to the definitions in Fig. 2(b). To resolve the meaning of s_o and s_d , and their relationship in

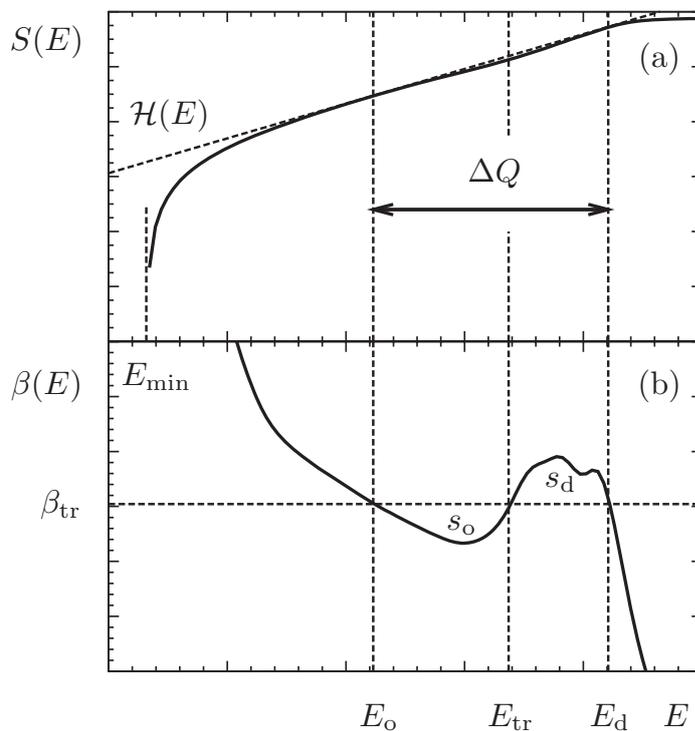


Figure 2. Microcanonical analysis by Maxwell construction: (a) Microcanonical entropy $S(E)$ and Gibbs construction $\mathcal{H}(E)$ as functions of energy E ; (b) Inverse thermal energy $\beta(E)$ and Maxwell line at the first-order transition point β_{tr} . The first-order-like transition behavior is characterized by the “backbending” effect between E_o and E_d . The Maxwell line intersects $\beta(E)$ at energies E_o , E_{tr} , and E_d . It is defined by the equality of the areas s_o and s_d which correspond to the surface entropy. These results were obtained by simulations of heteropolymer aggregation. Note the slight deformation of $\beta(E)$ right below E_d that indicates a subphase transition within the Maxwell regime, which cannot be considered separately in a microcanonical analysis based on Maxwell’s construction.

correspondence with the Maxwell construction, we calculate the difference of the value of the Gibbs hull and the entropy,

$$\Delta S(E) = \mathcal{H}(E) - S(E), \quad (8)$$

at the separation point E_{tr} :

$$\Delta S(E_{tr}) = S(E_o) + \beta_{tr}(E_{tr} - E_o) - S(E_{tr}) = S(E_d) + \beta_{tr}(E_{tr} - E_d) - S(E_{tr}), \quad (9)$$

where we made use of the two parametrizations of the Gibbs tangent given in Eq. (4). Since $\Delta S(E_{tr}) \neq 0$ is characteristic for first-order-like transitions in finite systems, where surface effects are not negligible, it is often called surface entropy, $\Delta S_{surf} \equiv \Delta S(E_{tr})$. Compared to the bulk of topological dimension D , the conformational entropic freedom at the surface of such systems is smaller, because of the reduced dimension $D - 1$. This has the effect that particles prefer to be part of the interior volume and not of the surface layer of the system. This results in shapes with minimal surfaces (e.g., spherical or globular conformations in an isotropic

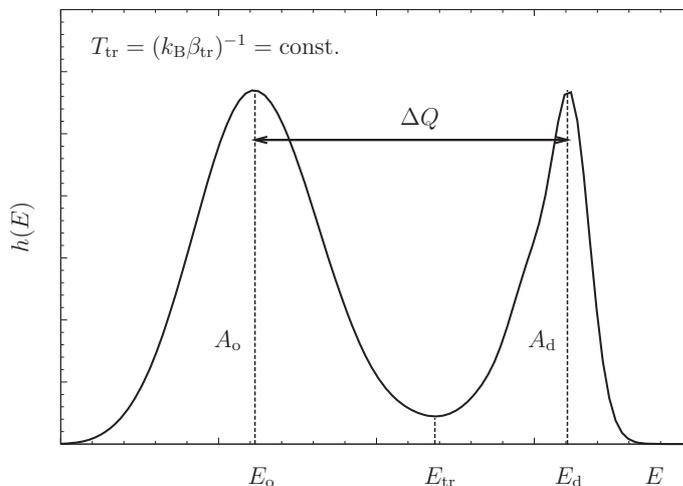


Figure 3. Canonical energy histogram at $T_{\text{tr}} = (k_B \beta_{\text{tr}})^{-1}$ of the same transition as identified in Fig. 2. Note that it is common to define $\beta \equiv 1/k_B T$ in the canonical analysis, whereas $\beta(E) \equiv 1/T(E)$ in the microcanonical theory.

medium). The “surface entropy” ΔS_{surf} is actually the amount of entropy suppression by the formation of surfaces. If the effective attractive interactions between the particles have a finite range, surface effects decrease with increasing system size (number of particles N) and such does ΔS_{surf} . For such systems, in the thermodynamic limit, $\lim_{N \rightarrow \infty} \Delta S_{\text{surf}} = 0$. Thus, in this limit, the entropy cannot be convex and thermodynamic first-order phase transitions do not exhibit this “backbending” feature that we discuss here in this section.

We eliminate $S(E_{\text{tr}})$ in Eq. (9) by employing Eqs. (6) and (7) and eventually find that

$$\Delta S_{\text{surf}} = s_o = s_d. \quad (10)$$

Thus, the Gibbs construction $\mathcal{H}(E)$ that corresponds to Maxwell’s line at β_{tr} , automatically leads to identical areas s_o and s_d and requires these areas to be identical to the surface entropy ΔS_{surf} . This is a remarkable result, as it shows that the surface entropy corresponds to the maximum deviation of the Gibbs tangent from the original $S(E)$ curve, located at E_{tr} . The transition point between the ordered and the disordered phase is well-defined by β_{tr} . Thus, the microcanonical analysis by Maxwell construction does not possess any ambiguity in the definition of transition points for finite systems, in contrast to the canonical analysis of peak positions and “shoulders” of fluctuations of typically not well-defined order parameters [1, 13].

The energy is considered here as an order parameter. It is not very specific (we do not learn much about the physical properties of the transition), but it allows us to clearly separate the phases. This is particularly apparent when falling back to the canonical interpretation of these features. Figure 3 shows the canonical histogram (unnormalized probability density distribution) $h(E) = g(E)e^{-E/k_B T_{\text{can}}}$ at the transition temperature $T_{\text{can}} = T_{\text{tr}}$ identified by Maxwell construction. This distribution has a characteristic bimodal form, with peaks at energies E_o and E_d , separated by the latent heat ΔQ . The minimum between the peaks is located at the separation point E_{tr} . Note that this approach defines the transition point at T_{tr} , where $h(E_o) = h(E_d)$. This is, as we have seen before, a direct consequence of the microcanonical analysis. The areas under the peaks in the ordered and in the coexisting disordered phase, A_o and A_d , respectively, are not necessarily identical.

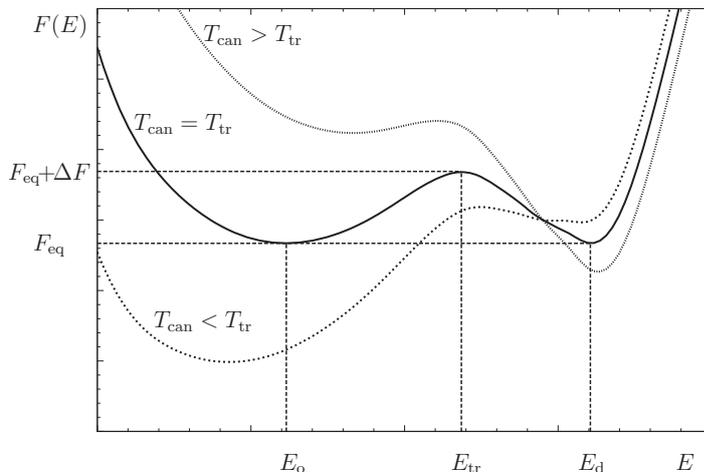


Figure 4. Free-energy profiles $F(E)$ for temperatures below, at, and above the transition point $T_{\text{can}} = T_{\text{tr}}$.

The histogram $h(E)$ represents the restricted partition sum of the system in energetic space,

$$h(E) \equiv Z_{\text{can}}^{\text{res}}(E) = \int dE' \delta(E - E') g(E') e^{-E'/k_{\text{B}}T_{\text{can}}}, \quad (11)$$

and T_{can} is a constant parameter representing the canonical temperature. Then, the free-energy landscape in energy space is parametrized by

$$F(E) = -k_{\text{B}}T_{\text{can}} \ln h(E) = E - T_{\text{can}}S(E). \quad (12)$$

Thermodynamically, only global minima in the free-energy landscape represent stable equilibrium states. The extremum condition $(dF/dE)_{E=E_{\text{ext}}} = 0$ thus yields

$$T(E_{\text{ext}}) = T_{\text{can}} \quad (13)$$

and connects the microcanonical and canonical pictures. Extrema in $h(E)$ at T_{can} are thus mirrored by extremal points in the $F(E)$ landscape, too. Because of the Maxwell construction, the transition point is defined by $T(E) = T_{\text{tr}}$. This is only satisfied at energies E_o , E_{tr} , and E_d , which, according to the condition (13) are also the locations of extremal points in the free-energy landscape at the transition point. In this interpretation, $F(E_o) = F_{\text{eq}}$ and $F(E_d) = F_{\text{eq}}$ represent the degenerate macrostates of the coexisting phases, and $F(E_{\text{tr}}) = F_{\text{eq}} + \Delta F$ is the free energy of the transition barrier. The height of the barrier, ΔF can be interpreted kinetically. Figure 4 shows free-energy profiles for temperatures below the transition point $T_{\text{can}} < T_{\text{tr}}$, where the system is in the ordered phase, at the microcanonically defined transition point $T_{\text{can}} = T_{\text{tr}}$, where the ordered and the disordered phases coexist, and above the transition temperature ($T_{\text{can}} > T_{\text{tr}}$). In the latter case, the free energy minimum lies beyond E_d , i.e., the system resides in the disordered phase.

Note that if one replaces in Eq. (12) the entropy $S(E)$ by its Gibbs hull in the transition regime,

$$F(E) = E - T_{\text{tr}}\mathcal{H}(E) = E_o - T_{\text{tr}}S(E_o) = E_d - T_{\text{tr}}S(E_d) \quad (14)$$

$$= F_{\text{eq}} = \text{const.} \quad \forall E \in [E_o, E_d]. \quad (15)$$

This is how the Maxwell construction affects the free-energy behavior: Each macrostate in the coexistence regime possesses the same free energy. This resembles the behavior of the Gibbs free energy in the liquid-gas coexistence regime of the van der Waals gas [see Fig. 1(b)]. Remember that in the latter case, the Maxwell construction was a physical necessity in the thermodynamic limit. In the microcanonical analysis for finite systems, we only made use of it to determine the transition point. We can therefore argue that the transition barrier $\Delta F > 0$ for the finite system is physical reality, but it disappears in the thermodynamic limit and the $F(E)$ curve converges to the Maxwell line. It is worth noting at this point, that the kinetics of processes such as protein folding is strongly affected by the existence of a transition barrier. Nonetheless, it is only a finite-size effect because of its surface-entropic origin.

The general disadvantage of the microcanonical analysis based on Gibbs/Maxwell construction is that it is only applicable to transitions with a clear, single signature, the “backbending effect”. Often, this is actually not the case. First-order transitions typically exhibit hierarchies of individual subphase transitions [1, 14]. A first indication can already be noticed in the example shown in Fig. 2(b), where an additional mini-backbending effect [6] can be observed between E_{tr} and E_d . In a systematic microcanonical analysis, such signals shall not be ignored. However, since this transition lies within the Maxwell coexistence regime, it cannot be resolved by this kind of analysis. Transitions without backbending feature, which we will later define as transitions of higher than first order, cannot be analyzed by Maxwell construction as well. In order to enable a thorough and systematic microcanonical analysis that includes hierarchies in first-order transitions and the identification of higher-order transitions, a revised theory is needed. A straightforward approach will be discussed in the following.

4. Systematic approach to the unique identification and classification of transitions in finite systems

As shown, the Maxwell construction can successfully be employed for the analysis of strong first-order transitions. Geometrically, the backbending region in the transition regime of the energetic temperature curve in Fig. 2 is replaced by an entirely flat segment. We also know that the backbending effect is due to surface effects that become negligible for very large systems, where volume properties are dominant. Thus, this flattening of the $\beta(E)$ curve is a physical property of this transition. It means that, in the transition region, the (volume part of the) system is not very sensitive to energetic changes. Macrostate changes require more energy (latent heat) while temperature changes decrease. The kinetics of macrostate changes is affected by the transition barrier. However, the Maxwell construction only applies to individual transitions of first order.

To include other transition types in the microcanonical analysis as well, it is attractive to extend the idea of a “flat” energetic region by replacing the Maxwell construction by a more general principle, the *principle of least sensitivity*, which dates back to the early days of classical mechanics. This is a weaker condition, but it allows us to investigate first- and higher-order transitions by a microcanonical analysis more systematically and in much more detail [1, 11].

This approach takes into account that all qualitative changes in the interplay of entropy and energy as signaled by alterations in the curvature of the microcanonical entropy $S(E)$, are indicators of cooperative behavior in the system. Since the complete phase behavior is already encoded in $S(E)$, the inverse microcanonical temperature $\beta(E)$ is considered to be the only unique parameter to identify transition points. The monotony of $\beta(E)$, as expressed by its derivative with respect to energy,

$$\gamma(E) = d\beta(E)/dE = d^2S/dE^2. \quad (16)$$

allows for the introduction of a systematic classification scheme of transitions in finite systems [11], but it can also be used for scaling analyses towards the thermodynamic limit. The function $\gamma(E)$ describes the variation of the inverse temperature with respect to energy

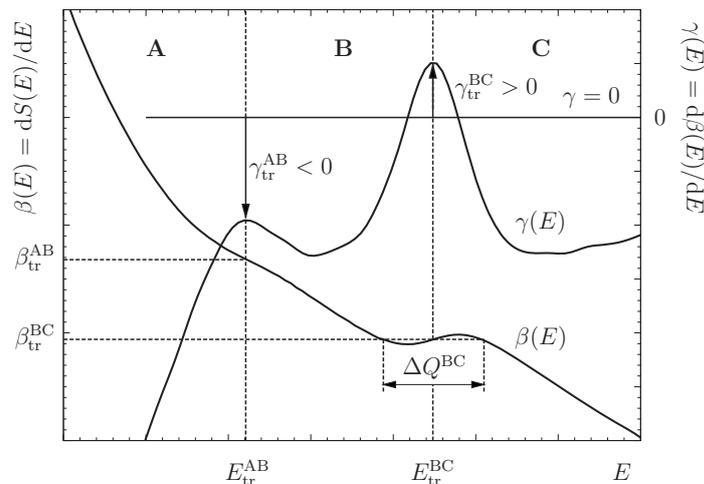


Figure 5. Inflection-point analysis of the inverse temperature $\beta(E)$ and its derivative $\gamma(E)$ as functions of energy E for a system exhibiting a first- and a second-order transition. The maxima of $\gamma(E)$ indicate transitions between the phases A and B at $E_{\text{tr}}^{\text{AB}}$ and B and C at $E_{\text{tr}}^{\text{BC}}$. The associated points $\beta(E_{\text{tr}}^{\text{AB}}) = \beta_{\text{tr}}^{\text{AB}}$ and $\beta(E_{\text{tr}}^{\text{BC}}) = \beta_{\text{tr}}^{\text{BC}}$ define the transition temperatures $T_{\text{tr}}^{\text{AB}} = (\beta_{\text{tr}}^{\text{AB}})^{-1}$ and $T_{\text{tr}}^{\text{BC}} = (\beta_{\text{tr}}^{\text{BC}})^{-1}$. According to the classification scheme of inflection-point analysis, the transition between A and B is of second order, since the slope of the inflection point is negative. On the other hand, B \leftrightarrow C is a first-order transition as the respective slope at $\beta(E_{\text{tr}}^{\text{BC}})$ is positive. The non-monotonic “backbending” is a characteristic signal of phase coexistence. The latent heat ΔQ^{BC} is defined as the energetic width of this transition region.

at a given energy value E . As such it is related with the microcanonical heat capacity via $C_V(E) = [dT(E)/dE]^{-1} = -\beta^2(E)/\gamma(E)$.

In this scheme, a transition between phases is defined to be of *first order* if the slope of the corresponding inflection point of $\beta(E)$ at $E = E_{\text{tr}}$ is positive,

$$\gamma_{\text{tr}} = \gamma(E_{\text{tr}}) > 0 : \text{first-order transition.} \quad (17)$$

Only in this case is the temperature curve non-monotonic and there is no unique mapping between β and E . As it has been discussed in the context of the Maxwell construction, this is the regime where both phases coexist. The overall energetic width of the undercooling, backbending, and overheating regions is identical to the latent heat. Thus, for a first-order transition, $\Delta Q > 0$. Note that the inflection point is not necessarily identical with the separation point obtained by Maxwell construction. A noticeable deviation between these energetic separation points is a strong indication that a subphase transition in one of the coexisting phases occurs. Such a transition cannot be detected by Maxwell construction only.

In the case that the inflection point has a negative slope, the phases cannot coexist and the latent heat is zero, $\Delta Q = 0$. In complete analogy to phase transitions in the thermodynamic limit, such transitions are classified as of *second order*:

$$\gamma_{\text{tr}} = \gamma(E_{\text{tr}}) < 0 : \text{second-order transition.} \quad (18)$$

Since the inflection points of $\beta(E)$ correspond to maxima in $\gamma(E)$, it is therefore sufficient to analyze the peak structure of $\gamma(E)$ in order to identify the transition energies and temperatures. The sign of the peak values classifies the transition. This very simple and general classification scheme applies to all physical systems.

Figure 5 illustrates the procedure for the identification of the transitions by means of inflection-point analysis. Plotted are the inverse temperature $\beta(E)$ and its energetic derivative $\gamma(E)$. There are two regions, where the weak-sensitivity condition applies to $\beta(E)$. One is located around the inflection point at $E_{\text{tr}}^{\text{AB}}$ and the other is the backbending regime surrounding the central inflection point at $E_{\text{tr}}^{\text{BC}}$. The latter exhibits the already well-described features of a first-order transition: $\gamma_{\text{tr}}^{\text{BC}}$ is positive and the intersection points of the inverse transition temperature $\beta_{\text{tr}}^{\text{BC}}$ with the $\beta(E)$ curve define the coexistence region. The width is interpreted as the latent heat, which is obviously nonzero: $\Delta Q^{\text{BC}} > 0$. The behavior is qualitatively different at $E_{\text{tr}}^{\text{AB}}$, where $\gamma_{\text{tr}}^{\text{AB}} < 0$. There is no phase coexistence so that the latent heat is zero. The $A \leftrightarrow B$ transition is consequently classified as a second-order transition. The transition point is given by the inverse temperature $\beta_{\text{tr}}^{\text{AB}}$.

In cases, where it is difficult to find first- or second-order traces of “hidden” finite-size effects in $\beta(E)$, the weak-sensitivity criterion can be extended by allowing higher-than-second-order transitions. This can be done by analyzing the inflection points of $\gamma(E)$, or if necessary, of even higher derivatives of $\beta(E)$. Therefore, our hierarchical analysis is an analog to the previously discussed Ehrenfest scheme in thermodynamics.

There is another issue worth being remarked. The consistency of the hierarchy $S \rightarrow \beta = dS/dE \rightarrow \gamma = d^2/dE^2 \rightarrow \dots$ tells us that, in principle, the *inverse* temperature β is more fundamental than the temperature T . This is not a trivial statement. Second-order transition points cannot easily be identified as inflection points of $T(E)$. The introduction of the temperature T (or, more precisely, $k_{\text{B}}T$) as a “measure” for thermal energy had merely occurred as a historical accident, but there were no substantial physical reasons to favor it. Microcanonical analysis based on the close relationship between entropy and *inverse* temperature suggests to consider β as the more appropriate thermodynamic variable.

5. Conclusion

As a general principle, one can conclude that cooperative behavior is encoded in the curvature of an appropriate “thermodynamic potential”. In the thermodynamic limit, one might want to choose to analyze phase transitions by means of canonical statistical analysis on the basis of the free energy. In the microcanonical analysis of small systems, it is the entropy as a function of energy that is considered to be the appropriate quantity. In the hierarchical inflection-point analysis, the variational principle standing behind the weak-sensitivity criterion tells us that first-order transitions are visible in the first derivative of $S(E)$ (backbending effect or Maxwell construction), second-order transitions are characterized by specific inflection points of $S(E)$, i.e., second-order derivatives are needed for their characterization, and higher-order transitions require higher-order derivatives to be identified. Inflection-point analysis is a simple but effective tool for a thorough and unique identification and classification of transitions in any physical system on all scales, from very small to very large.

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References

- [1] Bachmann M 2014 *Thermodynamics and Statistical Mechanics of Macromolecular Systems* (Cambridge: Cambridge University Press), in press
- [2] Thirring W 1970 *Z. Phys.* **235** 339
- [3] Janke W 1998 *Nucl. Phys. B* **63A-C** 631
- [4] Kastner M, Promberger M, and Hüller A 2000 *J. Stat. Phys.* **99** 1251
- [5] Gross D H E 2001 *Microcanonical Thermodynamics* (Singapore: World Scientific)

- [6] Junghans C, Bachmann M, and Janke W 2006 *Phys. Rev. Lett.* **97**, 218103
- [7] Hernández-Rojas J and Gomez-Llorente J M 2008 *Phys. Rev. Lett.* **100**, 258104
- [8] Junghans C, Bachmann M, and Janke W 2008 *J. Chem. Phys.* **128**, 085103
- [9] Taylor M P, Paul W, and Binder K 2009 *Phys. Rev. E* **79** 050801(R)
- [10] Taylor M P, Paul W, and Binder K 2009 *J. Chem. Phys.* **131** 114907
- [11] Schnabel S, Seaton D T, Landau D P, and Bachmann M 2011, *Phys. Rev. E* **84**, 011127
- [12] Gross J, Neuhaus T, Vogel T, and Bachmann M 2013, *J. Chem. Phys.* **138** 074905
- [13] Bachmann M and Janke W 2004 *J. Chem. Phys.* **120** 6779
- [14] Junghans C, Janke W, and Bachmann M 2011 *Comp. Phys. Commun.* **182** 1937