Thermodynamic interpretation of the uniformity of the phase space probability measure

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Abstract

Uniformity of the probability measure of phase space is considered in the framework of classical equilibrium thermodynamics. For the canonical and the grand canonical ensembles, relations are given between the phase space uniformities and thermodynamic potentials, their fluctuations and correlations. For the binary system in the vicinity of the critical point the uniformity is interpreted in terms of temperature dependent rates of phases of well defined uniformities. Examples of a liquid-gas system and the mass spectrum of nuclear fragments are presented.

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Introduction

Generalized entropies were proposed by Renyi [1] to characterize probability measures. Given a probability measure $d\mu$ and a partitioning of a phase space into $M(\cdot)$ cells, $f_i^{M(\cdot)}$, each of the same volume, the Renyi entropies $I_q(q \in \mathbb{R}^1)$ are defined

$$I_q = \begin{cases} \frac{1}{1-q} \ln \sum_{i=1}^{M(\cdot)} p_i^q; & q \neq 1 \\ -\sum_{i=1}^{M(\cdot)} p_i \ln p_i; & q = 1 \end{cases} \quad (1)$$

where

$$p_i = \frac{\int_{f_i^{M(\cdot)}} d\mu}{Z} \quad (2)$$

and sums run over cells for which $p_i \neq 0$. It has been found later by many authors [2] that for investigation of singular and multifractal measures a useful quantity is a
generalized dimension $D_q$, related to the Renyi entropy $I_q$

$$D_q = - \lim_{q \to 1} \frac{I_q}{\ln q} : \tag{3}$$

The Renyi dimension $D_q$ is always positive and decreases with $q$, so that there always exists $D_1 = \lim_{q \to 1} D_q$. For positive $q$, the $D_q$ and $I_q$ is mostly sensitive to these regions of the phase space where the measure is concentrated and for negative $q$ – where it is rarified.

In order to find a universal description of probability distributions for multifractals, another $q$-dependent quantity, called uniformity, was constructed by Beck in ref. [3] from Renyi dimensions or entropies

$$q = \frac{D_q + q(q-1)D_0}{D_q + (q-1)D_0} : \tag{4}$$

where $D_0$ stands for derivative over $q$. For all $q$, $0 < q < 1$. It can be found solving eq. (4) that for the most uniform probability density $q = 1$ and

$$D_q = D_1 : \tag{5}$$

does not depend on $q$. The minimum uniformity $q = 0$ corresponds to

$$D_q = \frac{1}{1-1/q}D_1 : \tag{6}$$

The derivative of the uniformity

$$q_0 = (q-1)\left[D_q D_0 + (1-q)D_0\right]$$

vanish for either $q = 1$, if it is differentiable there, or for

$$D_q = D_1 + \frac{D_0 - D_1}{1-q} : \tag{8}$$

The uniformity was introduced in order to characterize random variables on events generated by formal systems. It seems interesting to apply this concept to random variables related to physical systems in various conditions and represented by variables of thermodynamical ensembles. Since the probability measures for such ensembles are well defined and they determine both Renyi dimensions and all traditional thermodynamic potentials, the relations between these quantities should be easy to find. On this way one could expect to gain some understanding on how the structure of the phase space is reflected in such global characteristics of the system as its thermodynamic functions. Moreover, because of sensitivity of $D_q$ and
controlled by the parameter \( q \), to singularities of the measure, their relation to fluctuations of some measurable quantities, as internal energy or numbers of particles, or correlations of those, has to be straightforward. It can be also expected that two control parameters, the \( q \) for Renyi entropies and the temperature for thermodynamic potentials, should to some extent play similar roles in the formalism, the latter determining the strength of thermal fluctuations and the former steering the sensitivity of \( D_q \) and \( q \) to them.

**The Canonical Ensemble**

Consider the canonical ensemble with the probability measure

\[
d = \frac{1}{Z(\cdot)} e^{-E} dE
\]

where \( E \) stands for energy and

\[
Z(\cdot) = d
\]

is the partition function, where the integral is taken over the whole phase space, \( = 1/T \) is inverse temperature and the Boltzmann constant is assumed equal one. Using (1) we find for

\[
q \geq \frac{F(T/q) - F(T)}{T(1-q)} \quad q \notin 1
\]

\[
D_q \ln \geq \frac{\partial F(T)}{\partial T} = -S(T) \quad q = 1
\]

where

\[
F(T) = -T \ln Z(T)
\]

is free energy. Relation similar to (11), between Renyi entropies and free energy, was found by Tél in different context in ref. [4]. It is seen from eq. (11) that \( q \) is temperature scaling parameter. For \( q \notin 1 \) the Renyi entropy \( I_q \) is equal to the finite difference ratio of \( F \) and \( T \) and for \( q = 1 \) it becomes the usual relation between \( F \) and the thermodynamic entropy \( S \). Using (11), the uniformity (4) for the canonical ensemble is found

\[
\frac{1}{q} = \frac{1}{q} - \frac{F(T) - F(T=q)}{TS(T=q)}
\]

The maximum uniformity \( q = 1 \) corresponds to

\[
qF(T=q) = F(T) = -TS_{\text{max}}
\]
where $S_{\text{max}}$ is the maximum entropy. For the minimum uniformity, $q = 0$, the free energy $F$ does not depend on $q$ and

$$F(T=q) = F(T) = -TS_{\text{min}}; \quad q > 1$$

(15)

where $S_{\text{min}}$ is the minimum entropy.

Calculating the first and the second derivatives of $D_q$ and substituting to eq. \[7\] one finds

$$q(T) = \frac{1}{T-q} \frac{F(T=q) - F(T)}{U(T=q) - F(T)} V E(T=q);$$

(16)

where $V(E)$ is the variance of the energy $E$ and $U = hE$ is internal energy, or rewriting it in terms of the specific heat $c_V(T=q) = V [E(T=q)] = (T=q)^2$, using eq. \[13\] and formula $F = U - TS$

$$q(T) = \begin{cases} 0 & q < 1 \\ \frac{c}{hN(T=q)} \left( 1 - q \right)^2 \frac{E(T)}{(T-q)^2} & q > 1 \end{cases}$$

(17)

The Grand Canonical Ensemble

For the grand canonical ensemble the probability measure depends in addition on the number of particles $N$

$$d_N = \frac{1}{(\phi; c)} e^{-cN - E_N} dE_N$$

(18)

where $c$ is the chemical potential and $Z$ is the grand canonical sum

$$\left( \phi; c \right) = \sum_{N=0}^{\infty} d N :$$

(19)

The integral is taken over the whole $N$-particle phase space.

The Renyi dimensions in this case are \((! 0)\)

$$D_q \ln = \begin{cases} 0 & q \not\in 1 \\ \frac{\ln \left( T(T=q)^{i - N(T)} \right)}{i(T-q-1)} & q \not\in 1 \end{cases}$$

(20)

where the average number of particles is given by

$$hN(T) = \frac{T \ln (T; c)}{c}$$

(21)
and the uniformity is equal to
\[
\frac{1}{q} = \frac{1}{q} + \frac{\hat{h}N(T)i - hN(T=q)i}{\hat{h}N(T=q)TS(T=q)};
\]
(22)

Analogously to the canonical ensemble, the condition for the maximum uniformity is
\[
q\hat{h}N(T=q)i = hN(T)i = \frac{T}{c}S_{\text{max}}
\]
and for the minimum uniformity is
\[
hN(T=q)i = hN(T)i = \frac{T}{c}S_{\text{min}}; \quad q > 1;
\]
(23)

Calculating the first and the second derivatives of \(D_q\) one finds the derivative of \(q\)
\[
q_0(T) = \frac{1}{T-q} \frac{hN(T=q)i - hN(T)i}{\hat{h}N(T=q) + hN(T-q)i - hN(T)i}^2
\]
\(f\) \(\hat{h}N(T=q)i + \hat{V}[E(T=q)] - 2 \cdot \text{cov} \{\hat{h}N(T=q)i; E(T=q)\}\)
(25)

In case of constant volume and using eq. (20), the formula can be rewritten in the vicinity of \(q = 1\) in terms of the specific heat \(c_v\) and isothermal compressibility
\[
\hat{T}(T=q) = \hat{V}\{\hat{h}N(T=q)i\} - \hat{p}\hat{h}N(T=q)i
\]
(26)

\[
q_0(T) = \frac{(1-q)+T\hat{T}(T-q)}{T-qS(T-q) + \hat{c}N(T-q)i}\]
\(f\) \(cD(T-q)\hat{h}N(T=q)i + (T=q)^2c_v(T=q) - 2 \cdot \text{cov} \{\hat{h}N(T=q)i; E(T=q)\}\)

**Applications and Discussion**

The uniformity parameter \(q\) was originally proposed [3] to measure distance from the two extremes: the chaotic phase \((q = 1)\) and condensed phase \((q = 0)\).

We show in the following that for the system consisting of subsystems in thermal equilibrium, the overall uniformity is the weighted average of uniformities of subsystems with weights given by particle numbers ratios for subsystems.

Consider the two–phase system with average numbers of particles \(\hat{h}N(T)\) and the uniformities of pure phases \(U(T)\). In order to find the condition for \(U(T)\) to be independent of \(q\) one solves eq. (4)
\[
U(T) = \frac{D_1(T)q + q(q-1)D_0(T)q}{D_1(T)q + (q-1)D_0(T)q}
\]
(27)
with respect to $D_q$

$$
D_{1(2)q} = D_{1(2)1} \frac{q - i(2)}{q - 1}
$$

$$
D_{0(2)q} = D_{1(2)1} \frac{i(2) - 1}{(q - 1)^2};
$$

(28)

Using eq. (20) and the fact that chemical potentials in subsystems are equal in equilibrium, one finds

$$
D_q = D_{1q} + D_{2q}
$$

(29)

and, using (28),

$$
q(T; c) = c_1(T; c) + c_2(T; c)
$$

(30)

where

$$
c_{1(2)} = \frac{hN_{1(2)1}}{hN_{11} + hN_{21}}
$$

(31)

are concentrations of particles in subsystems 1 and 2. Generalization to more than two subsystems is straightforward.

**Example 1: classical liquid-gas system**

Consider any classical system of two coexisting phases in thermal equilibrium near the critical point. In the vicinity of critical temperature $T_c$, phase densities follow the power–law dependence on temperature [5]

$$
2 - 1 = \text{const} (T - T_c) ; \ T < T_c
$$

(32)

where $\gamma$ is the critical exponent (e.g. for the liquid-gas system its value is between 0.33 and 0.36). Assuming the average total number of particles $hN_1 + hN_2$ independent of temperature and the volume of the system to be constant, from eq. (32) follows that

$$
c_1 = A + B \left( 1 - \frac{T}{T_c} \right)
$$

$$
c_2 = 1 - c_1
$$

(33)

where $A$ and $B$ are constants. As discussed before, the parameter $q$ plays the role of the temperature scaling parameter. Thus the temperature evolution in eq. (33) can be rewritten in terms of $q = \frac{T}{T_c}$ [4]. Then $q = 1$ corresponds to the critical

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1The choice of $T_c$ as the reference is arbitrary but convenient. For another temperature scale one has to change the boundary conditions in eqns. (34).
temperature and domains \( q > 1 \) and \( 0 < q < 1 \) correspond to pure uniform (gas) and mixed phases, whereas the limit \( q = 0 \) should represent pure condensed (liquid) phase. For temperature \( T \) much lower than \( T_c \) there is only condensed phase in the system and a weak dependence of density on \( T \) can be neglected. Therefore, for \( q_0 = T = T_0 < 1 \), one finds the values of \( A \) and \( B \) from the limits

\[
\lim_{q \to 1^-} q = 1 \quad \lim_{q \to q_0^+} q = 2.
\]

Hence, from (33)

\[
c_1 = 1 - \frac{1}{1 - 2^{1-q}} = \frac{1 - q}{1 - q_0} \\
c_2 = 1 - \frac{1}{1 - 2^{1-q}} = \frac{1 - q}{1 - q_0}
\]

for \( q_0 < q < 1 \) and

\[
c_1(q_0) = 0 \\
c_2(q_0) = 1
\]

for \( q < q_0 \). The \( q \) does not have to be differentiable at \( q = 1 \).

The uniformity \( q \) for \( 0 < q < 1 \) and \( c_{1,2} \) given by (33) is shown in fig. 1. Since the power-law dependence of densities difference on temperature is valid for the near-to-critical region, this picture is realistic only for \( T \approx T_c \) or \( q ! 1 \) (see broken horizontal axis). However, if temperature dependence of phase densities is known for any temperature, the same line of reasoning can be followed to find the overall uniformity for the mixture of phases in wide range of temperatures. For some models, e.g. the power-law probability density mentioned in ref. [3], the uniformities of pure phases can be exactly calculated. In other cases, provided the probability measure is known, these pure uniformities can be also determined by direct, although sometimes complex and time consuming, computation. On the other hand, if the phase space probability density in the mixed-phase domain is measured experimentally and the uniformities of pure phases are known from elsewhere, or can be calculated, this theoretical scheme can be used to determine the ratio of phases at given temperature.

**Example 2: discrete power-law energy spectrum**

Let us discuss the system of discrete energy spectrum, where the energy \( E \) of the system is a random variable taking positive integer values and exhibiting the power-law probability measure

\[
dE = \frac{E^{-m}}{(E - m)dE}; \quad m = 1; 2; \ldots
\]
Figure 1: The uniformity $q$ for the two-phase system, assuming the near-to-critical power-law behaviour of densities difference as functions of temperature. Critical exponent $\gamma = 0.34$ is assumed.

where $(\cdot) = \prod_{m=1}^{\infty} m^{-1}$, $(\cdot > 1)$ is Riemann zeta function. Expected value of the energy is then

$$hE_i = \frac{(\cdot - 1)}{(\cdot \cdot)} \quad (38)$$

and exists only for $(\cdot > 2)$. Such statistical ensemble would be interesting per se and similar study of its properties in terms of Renyi entropy and Beck uniformity, as for the canonical and grand canonical ensembles, could be performed.

In order to stay within the framework of equilibrium thermodynamics and use the concept of equilibrium temperature, consider the canonical case. The statistical sum is equal to

$$Z(T) = \prod_{m=1}^{\infty} e^{-m^{-1}}$$

$$= \frac{1}{e^{1/T} - 1} \quad (39)$$

Internal energy is equal to

$$U(T) = -\frac{\partial \ln Z(T)}{\partial (1/T)}$$

$$= \frac{1}{1 - e^{-1/T}} \quad (40)$$
and by requiring it to be equal to $\hbar E_i$ we find the equilibrium temperature

$$T_{eq} = -\frac{1}{\ln (1 - \frac{1}{1-hE_i})}$$  \hspace{1cm} (41)$$

and the equilibrium probability measure

$$dE = \frac{(1 - \frac{1}{1-hE_i})^m}{hE_i - 1} \ (E - m) dE; \quad m = 1; 2; \ldots$$  \hspace{1cm} (42)$$

For this probability density we find

$$D_q (T_{eq}) \ln q < \begin{cases} \frac{1}{1-q} \ln [hE_i^q - (hE_i - 1)^q]; & q \neq 1 \\ (1 - hE_i) \ln (hE_i - 1) + hE_i \ln h \ i; & q = 1 \end{cases}$$  \hspace{1cm} (43)$$

and

$$q (T_{eq}) = \begin{cases} \frac{hE_i^q - (hE_i - 1)^q}{hE_i^{q+1} \ln (hE_i - 1)^q \ln (hE_i - 1)}; & q \neq 1 \\ 1; & q = 1 \end{cases}$$  \hspace{1cm} (44)$$

Table 1: Power-law exponents, temperatures, mean energies and uniformities for nuclear fragmentation data.

| $hE_i$ | $T\ M\ eV$ | $q = T/T_c$ | $q$ |
|-------|-------------|-------------|-----|
| 4.1   | 1.10        | 6.0         | 0.50| 0.29 | 0.05 |
| 3.8   | 1.14        | 6.2         | 0.52| 0.36 | 0.07 |
| 3.7   | 1.15        | 6.7         | 0.56| 0.49 | 0.08 |
| 3.0   | 1.37        | 7.2         | 0.60| 0.65 | 0.11 |
| 2.8   | 1.51        | 7.7         | 0.64| 0.75 | 0.12 |
| 3.2   | 1.28        | 8.2         | 0.68| 0.79 | 0.12 |
| 2.6   | 1.74        | 8.3         | 0.69| 0.83 | 0.13 |
| 2.4   | 2.21        | 14.0        | 1.16| 0.98 | 0.12 |
| 2.9   | 1.43        | 14.5        | 1.20| 0.96 | 0.11 |
| 2.9   | 1.43        | 15.0        | 1.25| 0.95 | 0.11 |

As an example of a real system exhibiting the power-law energy spectrum we employ the nuclear mass spectrum of heavy nuclei fragmentation. Taking simplifying assumptions that the whole energy is identical to the fragment mass, neglecting the surface energy, the binding energy and finite size effects and assuming that all states are distinguishable, we use the power-law exponents determined experimentally for low mass fragments and refered to in ref. [6]. The power-law behaviour is...
Figure 2: The uniformity \( q \) for experimental data from nuclear fragmentation. The dashed line represents analytical uniformity for \( \nu = 4:1 \) and the dotted one for \( \nu = 2:1 \).

also characteristic for liquid cluster size distribution near the liquid-gas transition point in real systems and in percolation models. It has to be noted however, that exponent obtained for nuclear systems disassembly [6] is not a universal critical exponent but an apparent exponent absorbing some temperature dependence, usually unknown. Nuclear data were analysed in ref. [6] in the framework of the condensation theory and the critical temperature \( T_c = 12.2 \pm 0.2 \) MeV was found. For each data sample exhibiting the power-law mass distribution the temperature was determined from either the slope of the energy spectrum at 90 or from the Fermi gas model or from the moving source model. We identify this temperature with the equilibrium temperature \( T = T_c \), define \( q = T/T_c \) and calculate \( q(T) \) from eq. (44). The numbers are given in tab. 1 and the uniformity as a function of \( q \) in fig. 2. For the calculation of errors of \( q \) the values for errors of \( T_c \), \( T \) and are taken from ref. [6]. The curves in fig. 2 represent uniformities calculated using analytical formula (44) for \( \nu = 2:4 \) and \( \nu = 4:1 \). As all experimental points stay within the belt determined by these curves we conclude that the temperature evolution given by (44) is consistent with data. The data show that uniformities increase with temperature in the mixed-phase region and are consistent with 1 above critical temperature. Below \( T = 4 \) MeV the contribution of the non-uniform phase is below 10%.
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