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2001 J. Phys. A: Math. Gen. 34 4663

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Thermodynamic interpretation of the uniformity of the phase space probability measure

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Received 19 February 2001

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.

PACS numbers: 0570, 6460

1. 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 $M(\Delta)$ cells, $\{\Delta_i\}_{i=1}^{M(\Delta)}$, each of the same volume Δ , the Renyi entropies I_q ($q \in R^1$) are defined as

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

where

$$p_i = \int_{\Delta_i} d\mu \quad (2)$$

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 by

$$D_q = - \lim_{\Delta \rightarrow \infty} \frac{I_q}{\ln \Delta}. \quad (3)$$

The Renyi dimension D_q is always positive and decreases with q , so that there always exists $D_\infty = \lim_{q \rightarrow \infty} D_q$. For positive q , the D_q (and I_q) is mostly sensitive to those regions of the phase space where the measure is concentrated and for negative q , to 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 [3] from Renyi dimensions or entropies:

$$\gamma_q = \frac{D_q + q(q-1)D'_q}{D_q + (q-1)D'_q} \quad (4)$$

where ' stands for derivative over q . For all q , $0 \leq \gamma_q \leq 1$. It can be found by solving equation (4) that for the most uniform probability density $\gamma_q = 1$ and

$$D_q = D_\infty \quad (5)$$

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

$$D_q = \frac{1}{1 - 1/q} D_\infty. \quad (6)$$

The derivative of the uniformity

$$\gamma'_q = (q-1) \frac{D_q[2D'_q - (1-q)D''_q]}{[D_q - (1-q)D'_q]^2} \quad (7)$$

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

$$D_q = D_\infty + \frac{D_0 - D_\infty}{1 - q}. \quad (8)$$

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 thermodynamic 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. In this way one could expect to gain some understanding of how the structure of the phase space is reflected in such global characteristics of the system as its thermodynamic functions. Moreover, because of the sensitivity of D_q and γ_q , controlled by the parameter q , to singularities of the measure, their relation to fluctuations of some measurable quantities, such as internal energy or numbers of particles, or correlations of those, has to be straightforward. It can also be 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 γ_q to fluctuations.

2. The canonical ensemble

Consider the canonical ensemble with the probability measure

$$d\mu = \frac{1}{Z(\beta)} e^{-\beta E} dE \quad (9)$$

where E stands for energy and

$$Z(\beta) = \int d\mu \quad (10)$$

is the partition function, where the integral is taken over the whole phase space, $\beta = 1/T$ is inverse temperature and the Boltzmann constant is assumed equal to one. Using (1) we find for $\Delta \rightarrow 0$

$$D_q \ln \Delta = \begin{cases} \frac{F(T/q) - F(T)}{T(1/q - 1)} & q \neq 1 \\ \frac{\partial F(T)}{\partial T} = -S(T) & q = 1 \end{cases} \quad (11)$$

where

$$F(T) = -T \ln Z(T) \quad (12)$$

is free energy. A relation similar to (11), between Renyi entropies and free energy, was found by T el in a different context in [4] but the following results of this paper are new. It is seen from equation (11) that q is the temperature scaling parameter. For $q \neq 1$ the Renyi entropy I_q is equal to the finite difference ratio of F and T and for $q \rightarrow 1$ it becomes the usual relation between F and the thermodynamic entropy S . Using (11), the uniformity (4) for the canonical ensemble is found by

$$\frac{1}{\gamma_q} = \frac{1}{q} - \frac{F(T) - F(T/q)}{TS(T/q)}. \quad (13)$$

The maximum uniformity $\gamma_q = 1$ corresponds to

$$qF(T/q) = F(T) = -TS_{\max} \quad (14)$$

where S_{\max} is the maximum entropy. For the minimum uniformity, $\gamma_q = 0$, the free energy F does not depend on q and

$$F(T/q) = F(T) = -TS_{\min} \quad q > 1 \quad (15)$$

where S_{\min} is the minimum entropy.

Calculating the first and the second derivatives of D_q and substituting into equation (7) one finds

$$\gamma'_q(T) = \frac{1}{T/q} \frac{F(T/q) - F(T)}{[U(T/q) - F(T)]^2} \mathcal{V}[E(T/q)] \quad (16)$$

where $\mathcal{V}(E)$ is the variance of the energy E and $U = \langle E \rangle$ is internal energy, or rewriting it in terms of the specific heat $c_V(T/q) = \mathcal{V}[E(T/q)]/(T/q)^2$, using equation (11) and the formula $F = U - TS$:

$$\gamma'_q(T) = \begin{cases} 0 & q > 1 \\ \frac{c_V(T/q)(1-q)S(T)}{[(1-q)S(T) - S(T/q)]^2} & q \rightarrow 1^- \end{cases} \quad (17)$$

3. The grand canonical ensemble

For the grand canonical ensemble the probability measure $d\mu_N$ depends, in addition, on the number of particles N :

$$d\mu_N = \frac{1}{\Xi(\beta, \mu_c)} e^{\beta[\mu_c N - E_N]} dE_N \quad (18)$$

where μ_c is the chemical potential and Ξ is the grand canonical sum

$$\Xi(\beta, \mu_c) = \sum_{N=0}^{\infty} \int d\mu_N. \quad (19)$$

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

The Renyi dimensions in this case are ($\Delta \rightarrow 0$)

$$D_q \ln \Delta = \begin{cases} \mu_c \frac{\langle N(T/q) \rangle - \langle N(T) \rangle}{T(1/q - 1)} & q \neq 1 \\ -\mu_c \frac{\partial \langle N(T) \rangle}{\partial T} = -S(T) & q = 1 \end{cases} \quad (20)$$

where the average number of particles is given by

$$\langle N(T) \rangle = T \frac{\partial \ln \Xi(T, \mu_c)}{\partial \mu_c} \quad (21)$$

and the uniformity is equal to

$$\frac{1}{\gamma_q} = \frac{1}{q} + \mu_c \frac{\langle N(T) \rangle - \langle N(T/q) \rangle}{TS(T/q)}. \quad (22)$$

Analogously to the canonical ensemble, the condition for the maximum uniformity is

$$q \langle N(T/q) \rangle = \langle N(T) \rangle = \frac{T}{\mu_c} S_{\max} \quad (23)$$

and for the minimum uniformity is

$$\langle N(T/q) \rangle = \langle N(T) \rangle = \frac{T}{\mu_c} S_{\min} \quad q > 1. \quad (24)$$

Calculating the first and the second derivatives of D_q one finds the derivative of γ_q :

$$\gamma'_q(T) = \frac{1}{T/q} \frac{\langle N(T/q) \rangle - \langle N(T) \rangle}{[U(T/q) - \mu_c(\langle N(T/q) \rangle - \langle N(T) \rangle)]^2} \times \{\mathcal{V}[\mu_c \langle N(T/q) \rangle] + \mathcal{V}[E(T/q)] - 2\mu_c \text{cov}[\langle N(T/q) \rangle, E(T/q)]\}. \quad (25)$$

In the case of constant volume and using equation (20), the formula can be rewritten in the vicinity of $q = 1$ in terms of the specific heat c_V and isothermal compressibility $\kappa_T(T/q) = \mathcal{V}[\langle N(T/q) \rangle]/p \langle N(T/q) \rangle$ and the correlation between these two quantities:

$$\gamma'_q(T) = \begin{cases} 0 & q > 1 \\ \frac{(1 - q/T)S(T)}{[T/q S(T/q) + \mu_c \langle N(T) \rangle]^2} \times \{\mu_c p \kappa_T(T/q) \langle N(T/q) \rangle + (T/q)^2 c_V(T/q) - 2\mu_c \text{cov}[\langle N(T/q) \rangle, E(T/q)]\} & q \rightarrow 1^- \end{cases} \quad (26)$$

4. Applications and discussion

The uniformity parameter γ_q was originally proposed [3] to measure distance from the two extremes: the chaotic phase ($\gamma_q = 1$) and the condensed phase ($\gamma_q = 0$). 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 number ratios for subsystems.

Consider the two-phase system with average numbers of particles $\langle N_{1(2)} \rangle$ and the uniformities of pure phases $\gamma_{1(2)}$. In order to find the condition for $\gamma_{1(2)}$ to be independent of q one solves equation (4):

$$\gamma_{1(2)} = \frac{D_{1(2)q} + q(q-1)D'_{1(2)q}}{D_{1(2)q} + (q-1)D'_{1(2)q}} \quad (27)$$

with respect to D_q :

$$D_{1(2)q} = D_{1(2)\infty} \frac{q - \gamma_{1(2)}}{q - 1} \quad D'_{1(2)q} = D_{1(2)\infty} \frac{\gamma_{1(2)} - 1}{(q - 1)^2}. \quad (28)$$

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

$$D_q = D_{1q} + D_{2q} \quad (29)$$

and, using (28),

$$\gamma_q(T, \mu_c) = c_1(T, \mu_c)\gamma_1 + c_2(T, \mu_c)\gamma_2 \quad (30)$$

where

$$c_{1(2)} = \frac{\langle N_{1(2)} \rangle}{\langle N_1 \rangle + \langle N_2 \rangle} \quad (31)$$

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

Example 1. Classical liquid–gas system

Consider the classical system of two coexisting phases, liquid and gas, 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]

$$\rho_2 - \rho_1 = \text{const} \cdot (T_c - T)^\alpha \quad T < T_c \quad (32)$$

where α is the critical exponent (for example, for the liquid–gas system its value is between 0.33 and 0.36). Assuming the average total number of particles $\langle N_1 + N_2 \rangle$ to be independent of temperature and the volume of the system to be constant, from equation (32) it follows that

$$c_1 = A + B \left(1 - \frac{T}{T_c}\right)^\alpha \quad c_2 = 1 - c_1 \quad (33)$$

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 equation (33) can be rewritten in terms of $q = T/T_c$. (The choice of T_c as the reference is arbitrary but convenient. For another temperature scale one has to change the boundary conditions in equations (34).) Then $q = 1$ corresponds to the critical temperature and domains $q \geq 1$ and $0 < q < 1$ correspond to pure uniform (gas) and mixed phases, whereas the limit $q = 0$ should represent the pure condensed (liquid) phase. For temperature T much lower than T_c there is only

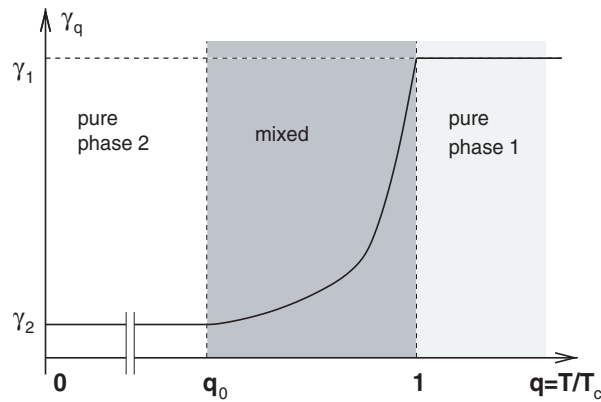


Figure 1. The uniformity γ_q for the two-phase system, assuming the near-to-critical power-law behaviour of densities difference as functions of temperature. Critical exponent $\alpha = 0.34$ is assumed.

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

$$\lim_{q \rightarrow 1^-} \gamma_q = \gamma_1 \quad \lim_{q \rightarrow q_0} \gamma_q = \gamma_2. \quad (34)$$

Hence, from equation (33),

$$c_1 = 1 - \frac{1}{1 - \gamma_2/\gamma_1} \left(\frac{1 - q}{1 - q_0} \right)^\alpha \quad c_2 = \frac{1}{1 - \gamma_2/\gamma_1} \left(\frac{1 - q}{1 - q_0} \right)^\alpha \quad (35)$$

for $q_0 \leq q < 1$ and

$$c_{1(2)} = 0 \quad c_{2(1)} = 1 \quad (36)$$

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

The uniformity γ_q for $\alpha = 0.34$ and $c_{1,2}$ given by (35) is shown in figure 1.

Since the power-law dependence of density difference on temperature is valid for the near-to-critical region, this picture is realistic only for $T \rightarrow T_c$ or $q \rightarrow 1$ (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 a wide range of temperatures. For some models (for example, the power-law probability density mentioned in [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 a given temperature.

Example 2. Discrete power-law energy spectrum

Let us discuss the system of a 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

$$d\mu_E = \frac{E^{-\tau}}{\zeta(\tau)} \delta(E - m) dE \quad m = 1, 2, \dots \quad (37)$$

where $\zeta(\tau) = \sum_{m=1}^{\infty} m^{-\tau}$ ($\tau > 1$) is the Riemann zeta function. The expected value of the energy is then

$$\langle E \rangle = \frac{\zeta(\tau - 1)}{\zeta(\tau)} \quad (38)$$

and it exists only for $\tau > 2$. Such a 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

$$\begin{aligned} Z(T) &= \sum_{m=1}^{\infty} e^{-m/T} \\ &= \frac{1}{e^{1/T} - 1}. \end{aligned} \quad (39)$$

Internal energy is equal to

$$\begin{aligned} U(T) &= -\frac{\partial \ln Z(T)}{\partial(1/T)} \\ &= \frac{1}{1 - e^{-1/T}} \end{aligned} \quad (40)$$

and by requiring it to be equal to $\langle E \rangle$, given by equation (38), we find the equilibrium temperature

$$T_{\text{eq}} = -\frac{1}{\ln(1 - 1/\langle E \rangle)} \quad (41)$$

and the equilibrium probability measure

$$d\mu_E = \frac{(1 - 1/\langle E \rangle)^m}{\langle E \rangle - 1} \delta(E - m) dE \quad m = 1, 2, \dots \quad (42)$$

For this probability density we find ($\Delta \rightarrow 0$)

$$D_q(T_{\text{eq}}) \ln \Delta = \begin{cases} -\frac{1}{1-q} \ln[\langle E \rangle^q - (\langle E \rangle - 1)^q] & q \neq 1 \\ (1 - \langle E \rangle) \ln(\langle E \rangle - 1) + \langle E \rangle \ln \langle M \rangle & q = 1 \end{cases} \quad (43)$$

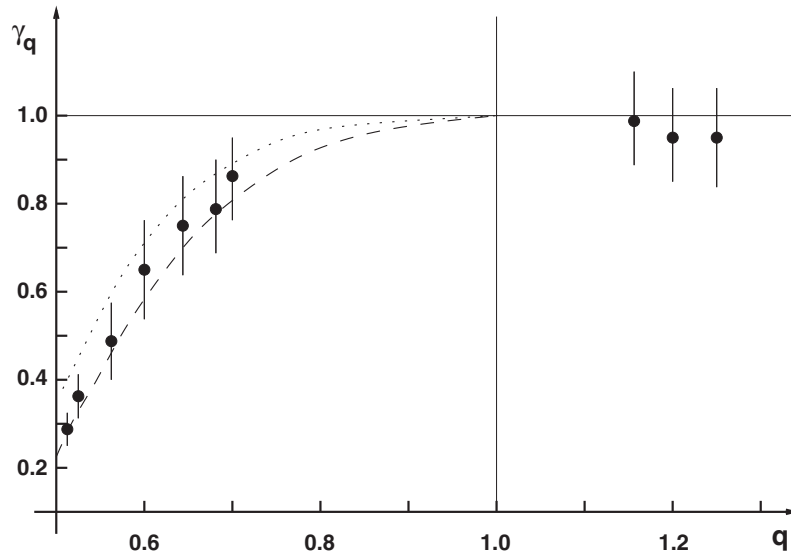
and

$$\gamma_q(T_{\text{eq}}) = \begin{cases} q - \frac{[\langle E \rangle^q - (\langle E \rangle - 1)^q] \ln[\langle E \rangle^q - (\langle E \rangle - 1)^q]}{\langle E \rangle^q \ln \langle E \rangle - (\langle E \rangle - 1)^q \ln(\langle E \rangle - 1)} & q \neq 1 \\ 1 & q = 1. \end{cases} \quad (44)$$

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 referred to in [6]. The power-law behaviour is 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 τ , as obtained for nuclear systems disassembly [6], is not a universal critical exponent but an apparent exponent absorbing some temperature dependence, usually unknown experimentally. Nuclear data were analysed in [6] in the framework of the condensation theory and the critical temperature $T_c = 12.0 \pm 0.2$ MeV was found. For each data sample exhibiting

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

τ	$\langle E \rangle$	T (MeV)	$q = T/T_c$	γ_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

**Figure 2.** The uniformity γ_q for experimental data from nuclear fragmentation. Dashed curve: analytical uniformity for $\tau = 4.1$; dotted curve: for $\tau = 2.1$.

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 (41), define $q = T/T_c$ and calculate $\gamma_q(T_{eq})$ from equation (44). The numbers are given in table 1 and the uniformity as a function of q in figure 2. For the calculation of errors of γ_q the values for errors of T_c , T and τ are taken from [6]. The curves in figure 2 represent uniformities calculated using analytic formula (44) for $\tau = 2.4$ and 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 the 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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