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Energy Fluctuations of Thermodynamic Systems: Higher Moments

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Accounts of the energy fluctuations of a thermodynamic system described by a canonical ensemble usually only deal with the second and occasionally with the third moment. This paper examines the nth moment for general values of n, with particular emphasis on the asymptotic limits in which either n or the particle number N or both become large.

1. INTRODUCTION

Expositions of the theory of the canonical ensemble customarily include accounts of the energy fluctuations of a thermodynamic system K represented by such an ensemble. Specifically it is shown that the second moment J_2, that is, the mean square deviation of the energy H from its mean is given by

$$J_2 := \langle (H-U)^2 \rangle = \langle U^2 \rangle - U^2 = kT^2C \tag{1}$$

Here ensemble means are indicated by broken brackets, $U := \langle H \rangle$ is the thermodynamic energy of K and C is its specific heat at constant deformation coordinates. Concomitantly the root mean square deviation of H from its mean U is

$$\sigma_2 := J_2^{1/2} = T(kC)^{1/2} \tag{2}$$

and the relative root mean square deviation is

$$\sigma_2^* := \sigma_2 / U \tag{3}$$

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In particular, when the energy of K is directly proportional to T, i.e., when $U = CT$ (C = const), $\sigma_2{}^*$ is constant:

$$\sigma_2{}^* = (k/C)^{1/2} \tag{4}$$

For example, a nonrelativistic assembly of N rigid, mutually noninteracting particles has the property in question and it has $C = \nu k$, where $\nu = \frac{1}{2}N(3+i)$, $i(=0,2,3)$ denoting the number of rotational degrees of freedom of a particle. In this case (4) reduces to

$$\sigma_2{}^* = \nu^{-1/2} \tag{5}$$

Occasionally (for example, Pathria, 1972) the "cubic analogs" of (1)–(5) are also considered, $J_3 := \langle (H-U)^3 \rangle$ being exhibited as a function of C, $\partial C/\partial T$, and T from which it then follows that under the conditions in which (5) obtains

$$\sigma_3{}^* := |J_3|^{1/3}/U = (2/\nu^2)^{1/3} \tag{6}$$

It would seem to be of interest to investigate the general case, that is to say, the nth moment

$$J_n := \langle (H-U)^n \rangle \tag{7}$$

$n = 0,1,2,3,\ldots$ and, where appropriate, the concomitant quantities

$$\sigma_n := |J_n|^{1/n}, \qquad \sigma_n{}^* := |J_n|^{1/n}/U \tag{8}$$

To this end, after introducing a generating function for the J_n in Section 2, a recurrence relation for the J_n is found in Section 3 with the aid of which the J_n may be obtained recursively. The case of particular interest in which $U = \nu kT (\equiv \nu/\beta)$ is considered generically in Section 4. Certain interesting polynomials $j_n(\nu)$ appear which are examined at some length in Section 5. Section 6 deals with various asymptotic limits: (i) $\nu \to \infty$, n fixed, (ii) $n \to \infty$, ν fixed, (iii) $n \to \infty$, ν/n fixed, the results obtained constituting one of the main objectives of this paper. In Section 7 general energy functions are considered, first under the assumption that they are regular in the range of temperatures of interest and then, briefly, when irregular behavior is admitted.

2. GENERATING FUNCTION FOR THE J_n

One has, directly from the definition (7),

$$J_n = \sum_{r=0}^{n} (-1)^r \binom{n}{r} U^{n-r} \langle H^r \rangle \tag{9}$$

If Z stands for the partition function or the sum over states, as the case may be,

$$\langle H^r \rangle = Z^{-1}(-\partial/\partial\beta)^r Z \tag{10}$$

In particular,

$$U = -Z'/Z \tag{11}$$

primes denoting derivatives with respect to β. Hence $\langle H^r \rangle$ and therefore J_n express themselves in terms of the derivatives of U alone. However, the process of finding the explicit expressions for the J_n by inserting (10) in (9) contains much redundancy in the sense that a very large number of terms which appear on the right of (10) eventually mutually cancel from the sum on the right of (9). For this and other reasons it is better to proceed as follows. Define

$$J := \sum_{n=0}^{\infty} (-1)^n J_n x^n / n! \tag{12}$$

where x is an auxiliary variable. Then, using (7) on the right,

$$J = \langle e^{-x(H-U)} \rangle = e^{xU} \langle e^{-xH} \rangle$$

Therefore, by inspection

$$J = e^{xU(\beta)} Z(\beta + x)/Z(\beta) \tag{13}$$

By means of (11) this may be written in terms of U alone:

$$J = \exp\left[xU(\beta) - \int_0^x U(t+\beta)\, dt \right] \tag{14}$$

Writing $U(t+\beta)$ as a series in ascending powers of t, one also has

$$J=\exp\left(-\sum_{s=2}^{\infty} U_{s-1}x^s/s!\right) \tag{15}$$

where $U_s := (\partial/\partial\beta)^s U(\beta)$.

3. RECURRENCE RELATION: J_n FOR $2 \leqslant n \leqslant 8$

Differentiating $\ln J$, as given by (14), alternatively with respect to β and x one obtains the relation

$$\partial J/\partial\beta - \partial J/\partial x = xU_1 J$$

Inserting for J the series (12), there follows the recurrence relation

$$J_{n+1} = -J_n' - nU_1 J_{n-1} \tag{16}$$

Use of this leads easily to the following explicit expressions, starting with $J_0=1$, $J_1=0$:

$$\begin{aligned}
&J_2=-U_1, \qquad J_3=U_2, \qquad J_4=-U_3+3U_1^2\\
&J_5=U_4-10U_1U_2, \qquad J_6=-U_5+15U_1U_3+10U_2^2-15U_1^3\\
&J_7=U_6-21U_1U_4-35U_2U_3+105U_1^2U_2\\
&J_8=-U_7+28U_1U_5+56U_2U_4+35U_3^2-210U_1^2U_3-280U_1U_2^2+105U_1^4
\end{aligned} \tag{17}$$

and so on. The J_n thus appear explicitly as functions of the derivatives of U alone. For general n some results concerning the expression for J_n will be found in Section 7.

4. THE CASE $U=\nu/\beta$: GENERIC RESULTS

So far everything has been general: the only condition which has implicitly been imposed being that the various derivatives of U should in fact exist. At this point is is of advantage to deal at some length with a particular case, namely, when $U=\nu/\beta$, where ν is a constant. The energy of a classical (nonrelativistic) ideal gas has this form (cf. Section 1) as has the extreme-relativistic Maxwell–Jüttner gas, for which $\nu=3N$.

Equation (14) now takes the explicit form

$$J=(1+\xi)^{-\nu}e^{\nu\xi} \tag{18}$$

with $\xi := x/\beta$. Evidently

$$J_n = j_n\beta^{-n} \tag{19}$$

where j_n is a constant factor. [When its dependence on ν requires emphasis I shall write $j_n(\nu)$ for it.] Inserting (19) in (16), one finds that the j_n satisfy the linear recurrence relation

$$j_{n+1}=n(j_n+\nu j_{n-1}) \tag{20}$$

The quantities $\sigma_n{}^*$ defined earlier are here independent of β. In fact,

$$\sigma_n{}^*(\nu)=\nu^{-1}[j_n(\nu)]^{1/n} \tag{21}$$

5. THE POLYNOMIALS $j_n(\nu)$

Since $j_0=1$ and $j_1=0$ the polynomials $j_n(\nu)$ may be generated recursively from (20). Thus

$$\begin{aligned}
&j_2=\nu, \qquad j_3=2\nu, \qquad j_4=6\nu+3\nu^2, \qquad j_5=24\nu+20\nu^2\\
&j_6=120\nu+130\nu^2+15\nu^3, \qquad j_7=720\nu+924\nu^2+210\nu^3\\
&j_8=5040\nu+7308\nu^2+2380\nu^3+105\nu^4
\end{aligned} \tag{22}$$

and so on. That these are correct may be verified by substitution in the relation

$$j_n(\mu+\nu)=\sum_{r=0}^{n}\binom{n}{r}j_{n-r}(\mu)j_r(\nu) \tag{23}$$

which follows directly from (18). Again, formally setting $\nu=-1$ in (18), one infers that $j_n(-1)=1-n$, in harmony with (22).

An integral representation for $j_n(\nu)$ may be obtained by writing the factor $(1+\xi)^{-\nu}$ in (18) as $[\Gamma(\nu)]^{-1}\int_0^\infty t^{\nu-1}e^{-(1+\xi)t}\,dt$. Thus

$$\Gamma(\nu)j_n(\nu)=\int_0^\infty t^{\nu-1}(t-\nu)^n e^{-t}\,dt \tag{24}$$

By splitting the range of integration at $t=\nu$ it follows that

$$\Gamma(\nu)j_n(\nu)=\nu^{n+\nu}\left[\int_1^\infty t^{\nu-1}(t-1)^n e^{-\nu t}\,dt+(-1)^n\int_0^1 t^{\nu-1}(1-t)^n e^{-\nu t}\,dt\right] \tag{25}$$

a result which will prove useful later. One remarkable special case of this (Abramowitz and Stegun, 1970) deserves special mention:

$$j_{n-1}(n)=\pi^{-1/2}n^{n-1/2}e^{-n/2}\left[K_{n-1/2}(\tfrac{1}{2}n)+(-1)^{n-1}\pi I_{n-1/2}(\tfrac{1}{2}n)\right] \tag{26}$$

where I_r and K_r are modified Bessel functions of the first and second kind which are here, of course, just those which are in fact elementary functions. More generally, the integrals in (25) are familiar from the theory of confluent hypergeometric functions (e.g., reference 2, p. 505). However, upon introducing them explicitly one is faced with quite awkward manipulations. In any event, elementary methods are more suited to our purpose and they suffice for its attainment.

First, by writing both factors on the right of (18) as power series, one infers that

$$j_n(\nu)=\sum_{r=0}^{n}(-1)^r\binom{n}{r}q_{n-r}(\nu)\nu^r \tag{27}$$

where $q_r(\nu)=\Gamma(r+\nu)/\Gamma(\nu)$. $q_r(\nu)$ is a polynomial of degree r in ν which can be written out explicitly in terms of Stirling numbers of the first kind. This does not seem to be useful since according to (27) $j_n(\nu)$ superficially has the appearance of being a polynomial of degree n, whereas it is in fact of degree $m=[\frac{1}{2}n]:=$integral part of $\frac{1}{2}n$. Thus

$$j_n(\nu)=\sum_{k=1}^{m}j_{nk}\nu^k \tag{28}$$

This may be inserted into (20) to obtain recursion relations for the j_{nk}:

$$j_{n+1,k}=n(j_{nk}+j_{n-1,k-1}),\qquad k>1 \tag{29}$$

and $j_{n1}=(n-1)!$ Then

$$j_{n2}=(n-1)!\sum_{j=2}^{n-2}1/j,\qquad j_{n3}=(n-1)!\sum_{k=4}^{n-2}\sum_{j=2}^{k-2}1/jk \tag{30}$$

and so on. This method is, however, not suitable for getting the descending sequence of coefficients $j_{nm}, j_{n,m-1}, \ldots$ owing to the need now to distinguish generically between even and odd values of n: one has in effect two interrelated recursion relations which are not easily dealt with. It is far easier to proceed as follows. If $w := \xi - \ln(1+\xi)$,

$$J = e^{\nu w} = \sum_{p=0}^{\infty} \nu^p \left[\sum_{s=2}^{\infty} (-\xi)^s / s \right]^p / p! \tag{31}$$

After writing w^p explicitly as a series in ascending powers of ξ, select from the terms with $p = m, m-1, \ldots$ in turn the factors multiplying ξ^n; and these are just $j_{nm}, j_{n,m-1}, \ldots$, respectively. In this way one finds that, when n is even

$$j_{nm} = n!/2^m m!, \qquad j_{n,m-1} = \tfrac{1}{36} n(n-2)(2n+1) j_{nm}$$

when n is odd,

$$j_{nm} = \tfrac{1}{3}(n!)/2^{m-1}(m-1)!, \qquad j_{n,m-1} = \tfrac{1}{540}(n-3)(10n^2 + 15n - 1) j_{nm} \tag{32}$$

and so on. When $n \gg 1$ $j_{n,m-1}/j_{nm} = O(n^3)$ and it is not difficult to convince oneself that $j_{n,m-2}/j_{n,m-1}$ is likewise $O(n^3)$, and so on.

6. ASYMPTOTIC RESULTS

It is of interest to examine the asymptotic form of $j_n(\nu)$ and its concomitant σ_n^* under various circumstances.

(a) ν Large, n Fixed. For fixed n the dominant term of $j_n(\nu)$ is $\alpha_n \nu^m$, where $\alpha_n := j_{nm}$, if only ν is sufficiently large. Thus, bearing in mind the results obtained at the end of Section 5,

$$j_n(\nu) = \alpha_n \nu^m \left[1 + O(n^3/\nu) \right] \tag{33}$$

and therefore, as $\nu \to \infty$ with n fixed,

$$\sigma_n^* \sim \alpha_n^{1/n} \times \begin{cases} \nu^{-1/2} & (n \text{ even}) \\ \nu^{-1/2}(1 + 1/n) & (n \text{ odd}) \end{cases} \tag{34}$$

When n is also large, i.e.,

$$1 \ll n \ll \nu^{1/3} \tag{35}$$

Stirling's formula may be used to find the asymptotic form of $\alpha_n^{1/n}$:

$$\alpha_n^{1/n} \sim (n/e)^{1/2} \times \begin{cases} 1 + O(n^{-1}), & n \text{ even} \\ 1 + O(n^{-1} \ln n), & n \text{ odd} \end{cases} \tag{36}$$

Retaining explicitly only the leading term it follows that subject to (35)

$$\sigma_n^*(\nu) \sim (n/e\nu)^{1/2} \tag{37}$$

(34) and (37) are relevant when one contemplates a macroscopic sample of an ideal gas, say one mole, for then the condition $n^3/\nu \ll 1$ merely requires n to be small compared with 10^8.

(b) *n* Large, *ν* Fixed. Writing out the series on the right of (27) explicitly, one recognizes by inspection that when $n \to \infty$ with ν fixed

$$\Gamma(\nu) j_n(\nu) \sim \Gamma(n+\nu) e^{-\nu} (1 + a_1 n^{-1} + a_2 n^{-1} + \cdots) \tag{38}$$

where a_k is a polynomial of degree $2k$ in ν. The a_k may be determined recursively by substituting (38) in (20). Thus

$$a_1 = \nu(\nu - 1), \qquad a_2 = \tfrac{1}{2}\nu(\nu - 1)(\nu^2 - 4\nu + 2), \ldots \tag{39}$$

It may be noted that when $\nu = 1$ all the a_k vanish. This means that $f_n = n!/e$ is an exact solution of the difference equation $f_{n+1} = n(f_n + f_{n-1})$. However, the general solution of this second-order equation is

$$f_n = (n!) \left[A + B \sum_{r=n+1}^{\infty} (-1)^r / r! \right] \tag{40}$$

and in the present context the arbitrary constants A and B are determined by the initial conditions $f_0 = 1, f_1 = 0$, i.e., $A = e^{-1}, B = -1$. This result is not in conflict with (38) since the second term on the right of (40) is $O(1/(n+1)!)$.

Bearing in mind that $n \gg 1$, $\Gamma(n + \nu)$ may be replaced by the leading term of Stirling's formula, so that

$$\Gamma(\nu) j_n(\nu) \sim (2\pi)^{1/2} n^{n+\nu-1/2} e^{-n-\nu} \tag{41}$$

Therefore, subject to $\nu^2 \ll n$,

$$\sigma_n^*(\nu) \sim n/e\nu \tag{42}$$

(c) *n* and *ν* Comparable. Suppose now that $\nu = \lambda n$, where λ is a fixed number. To find $j_n(\lambda n)$ when $n \to \infty$ the preceding methods fail. In this case one may appeal to (25) directly, using the following well-known result (Erdelyi, 1956). If $f(t)$ has one steep minimum at $t = t_0$ $(a < t_0 < b)$ then

$$\int_a^b e^{-f(t)}\,dt \sim e^{-f(t_0)}\left[2\pi/f''(t_0)\right]^{1/2} \tag{43}$$

Here

$$f(t) = \lambda n t - (\lambda n - 1)\ln t - n \ln|t-1| \tag{44}$$

For large values of n each of the integrands in (25) has just one steep minimum within the respective ranges of integration:

$$t_0 = 1 + \left[1 \pm (4\lambda+1)^{1/2}\right]/2\lambda + O(n^{-1}) \tag{45}$$

the upper and lower signs referring to the first and second integral, respectively. Then the second integral is negligible compared with the first. If

$$c := \tfrac{1}{2}\left[1 + (1+4\lambda)^{1/2}\right] \tag{46}$$

(45) becomes correctly to $O(n^{-2})$

$$t_0 = \left[c/(c-1)\right] - n^{-1}/\left[(c-1)(2c-1)\right] \tag{47}$$

This value of t is now to be substituted on the right of (43). Using the usual asymptotic formula for $\Gamma(\lambda n)$, one obtains the result

$$j_n(\lambda n) \sim \left[(c-1)/(2c-1)\right]^{1/2}\left\{c\left[c/(c-1)\right]^{c(c-1)}e^{-c}n\right\}^n \tag{48}$$

Hence

$$\sigma_n^*(\lambda n) \sim (c-1)^{-1}\left[c/(c-1)\right]^{c(c-1)}e^{-c} \tag{49}$$

In particular,

$$\sigma_n^*(n) \sim (1+2\rho)e^{-\rho} \tag{50}$$

where ρ is the "golden ratio" $\frac{1}{2}(1+\surd 5)$.

Remark. In the limits $\lambda \to \infty$ and $\lambda \to 0$ (49) reduces exactly to (37) and (42), respectively. One suspects that $\sigma_n^*(\nu)$ is asymptotically represented by the right-hand member of (49) for all values of ν and n when both are sufficiently large. This conjecture is borne out by the results of explicit calculation.

7. MORE GENERAL ENERGY FUNCTIONS

The preceding three sections have concerned themselves with the particular case $U=\nu/\beta$. Going on to more general energy functions, it will be required for the time being that for any given value of β of interest the function $U(\beta)$ is analytic within and on a circle Γ of radius $R(\beta)$ with β as center.

If, as before, N is the number of distinct systems ("particles") which constitute the assembly, U is proportional to N in the thermodynamic limit. For any realistic macroscopic assembly—which alone I consider now—N is very large indeed compared with unity and it is legitimate to take $U=O(N)$. Accordingly write $U=:Nu$ and $|U_s|=:Nu_s$, with $u=O(1)$ and $u_s=O(1)$.

To find the dominant terms of J_n one may proceed as after (31):

$$\sum_{n=0}^{\infty}(-1)^n J_n x^n/n! = \sum_{p=0}^{\infty}(-1)^p w^p/p! \tag{51}$$

where now

$$w := \sum_{s=2}^{\infty} U_{s-1}x^s/s!$$

Write

$$w^p = \left(\tfrac{1}{2}U_2x^2\right)^p \sum_{r=0}^{\infty} c_r(p)x^r \tag{52}$$

so that, for example, $c_1(p)=pU_2/3U_1$. By inspection one thus arrives at the following results:

(i) when n is even,

$$J_n=(-1)^m\alpha_n\{U_1{}^m-\tfrac{1}{72}n(n-2)U_1{}^{m-3}[3U_1U_3+(n-4)U_2^2]+\cdots\} \quad (53)$$

(ii) when n is odd,

$$J_n=(-1)^{m+1}\alpha_n\{\tfrac{1}{2}U_1{}^{m-1}U_2-\tfrac{1}{2160}(n-3)U_1{}^{m-4}$$
$$[45(n-5)U_1U_2U_3+5(n-5)(n-7)U_2^3+54U_1{}^2U_4]+\cdots\} \quad (54)$$

Evidently the successive group of terms are in each case $O(N^m)$, $O(N^{m-1}), O(N^{m-2}),\ldots$, so that when N is sufficiently large each sequence is dominated by its first term. Therefore, as $N\to\infty$, with n and β fixed,

$$\sigma_n{}^*(\beta)\sim\alpha_n{}^{1/n}(u_1/u^2)^{1/2}\times\begin{cases}N^{-1/2}, & n\text{ even}\\ (\tfrac{1}{4}u_2{}^2/u_1{}^3)^{1/2n}N^{-(1+1/n)/2}\end{cases} \quad (55)$$

which may be compared with (34). If n is itself large but not too large (see below)

$$\sigma_n{}^*(\beta)\sim(nu_1/eu^2N)^{1/2} \quad (56)$$

cf. (37).

It remains to investigate the conditions which N and n must satisfy if the right-hand members of (55) and (56) are to be adequate approximations to $\sigma_n{}^*(\beta)$. Accordingly, let the upper bound of u on Γ be $\mu(\beta)$. Then by Cauchy's inequality

$$u_s\leqslant(s!)\mu R^{-s} \quad (57)$$

Taking n even, $n>2$, if ρ is the magnitude of the ratio of the second term to the first on the right of (53), it follows that

$$\rho<\rho_1:=\tfrac{1}{18}n^3(\mu^2u_1{}^3R^4)N^{-1} \quad (58)$$

Hence $\rho\ll 1$ provided

$$n^3/N\ll 18R^4u_1{}^3/\mu^2 \quad (59)$$

When n is odd one may deal with (54) in much the same way. The condition analogous to (59) turns out to be

$$n^3/N \ll 27R^6 u_1^{\,3} u_2/\mu^3 \tag{60}$$

It is convenient to have an inequality which covers the cases of even and odd n simultaneously. Accordingly, weaken (58) by multiplying its right-hand member by $R^2 u_2/2\mu < 1$. Then for any $n > 2$, $\rho \ll 1$ when

$$n \ll \eta N^{1/3}, \qquad \eta^3 := 9R^6\mu^{-3}u_1^{\,3}u_2 \tag{61}$$

This is thus a necessary condition for the right-hand member of (55) to be an adequate approximation of $\sigma_n{}^*(\beta)$. Presumably it is also sufficient, but to establish this in generality would not be easy. It is, however, worthy of remark that the ratio of the magnitude of the third term on the right of (54) to that of the first is less than $\frac{1}{6}\rho_1^{\,2}$.

As regards the transition from (55) to (56), one has to have $n \gg \frac{1}{2}\ln N$ if the factor $N^{-1/2n}$ is to be negligible. Satisfaction of this condition ensures at the same time that $(n/e)^{1/2}$ be a sufficiently good approximation of $\alpha_n{}^{1/n}$. There remains the condition $|\frac{1}{2}\ln(u_2^{\,2}/4u_1^{\,3})| \ll n$. The left-hand member being independent of N, conflict with (61) will not arise if only N is sufficiently large.

When using (61) one will aim at the largest possible value of η. In any particular case one will therefore find μ as a function of R and then choose that value of the latter which maximizes R^2/μ. For example, when u is proportional to $\beta^{-\lambda}$, with λ a positive constant, R^2/μ is proportional to $R^2(\beta - R)^\lambda$, so that the most favorable value of R is then $2\beta/(\lambda+2)$.

When the assumption of regularity is relaxed the results so far obtained in this section generally become irrelevant in a neighborhood of any value β_c of β at which the behavior of U is pathological. What one usually encounters in practice is this: for some positive integer r, the derivatives of U beyond the rth are unbounded as $\varepsilon := |\beta_c - \beta| \to 0$. In that case, when $n > r+1$, J_n will be dominated by the last term $(-1)^{n-1}U_{n-1}$ on the right of (53), (54) if only ε is sufficiently small; so that then $|J_n| \sim N u_{n-1}$. When, specifically, C is proportional to $\varepsilon^{-\lambda}$, where λ is a positive constant (cf. reference 1, p. 432), it turns out that

$$\sigma_n{}^*(\beta) \sim \gamma(n)(N^{-1}\varepsilon^{-(2-\lambda)})^{(1-1/n)}, \qquad \varepsilon \to 0 \tag{62}$$

The factor $\gamma(n)$ depends on n alone and is proportional to n when n is sufficiently large. No matter how large N may be, $\sigma_n^*(\beta)$ diverges as $\beta \to \beta_c$.

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