

## Statistical theory of an adiabatic process

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Within the existing phenomenological theory of an adiabatic process it is implicit that the system is characterized by a temperature at any moment. However, since in this process there is no thermostat, the probability distribution in general would not be canonical. In this paper we find the distribution corresponding to an adiabatic process, being based on the commonly accepted statement that the equilibrium state of a system with a fixed energy is the one characterized by the microcanonical distribution. We show that (i) for a system with constant heat capacity, which is typical in the classical limit, the distribution in an adiabatic process is canonical, despite the absence of thermostat, and (ii) in the general case the mean value of energy in the thermodynamic limit for an adiabatic process is the same as that calculated using the canonical distribution, but its fluctuation is different.

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### I. INTRODUCTION

In the commonly accepted approach, the statistical theory of all equilibrium thermodynamic processes is based on the relation between the free energy and the partition function  $F = -T \ln Z$ , which implies the presence of the Gibbs canonical distribution. The latter takes place for a system in a thermostat. At the same time, in the case of an adiabatic process, i.e., a process in an adiabatically isolated system, the thermostat is absent. Therefore, within statistical theory, the adiabatic process demands special consideration.

Indeed, in accordance with the aforesaid, in the existing statistical theory there is the consideration of a process which can be naturally called *zero polytropic*: the thermostat is *present* (because the distribution is canonical), but  $\delta Q = 0$ , so that the heat capacity  $c = 0$ , hence the name. The results are transferred onto the case of the “true” adiabatic process (for which  $\delta Q = 0$  due to the absence of thermostat); however, not only is the fact of such transference ignored, but also the understanding of the existence of two *a priori* different processes—zero polytropic and adiabatic—is absent.

In statistical thermodynamics a process is characterized by a family of distributions. In each point of a zero-polytropic curve the distribution is canonical; but for an adiabatic curve this is by no means obvious—and in general not true. In order to find the distribution corresponding to a point of an adiabatic curve, an evolution equation is needed, which should in principle follow from the underlying dynamical equations. The equations, generally speaking, are not known. However, it is accepted

that a system with fixed energy, left by itself, eventually comes into an equilibrium state characterized by the microcanonical distribution. One can conclude that the evolution of the probability distribution is essentially the equalization of probabilities within energy levels. If levels cross as a result of changing external parameters, there should be such equalization at each crossing, provided the process is slow enough that there is time for the equilibrium to be reached. Otherwise the probabilities are to remain constant for each level due to the adiabatic theorem.

Accepting the above picture and given the dependence of the whole spectrum on the external parameter(s), one can find the adiabatic distribution. Here we will carry out an extended consideration and compare the results for the adiabatic and zero-polytropic processes. The rest of the paper is organized as follows. Section II is devoted to a detailed discussion of the definitions of the two processes. In Sec. III we recite the microcanonical postulate, which is essentially equivalent to the common statement that a system by itself comes into a microcanonical state. Section IV describes how the probability distribution behaves in an adiabatic process being based on this postulate. In Sec. V the quasicontinuous spectrum approximation is introduced and the equation for the distribution is derived. This has the form of a wave equation; its solution is constructed in Sec. VI and the question about when it coincides with the zero-polytropic (canonical) distribution is addressed in Sec. VII. Sections VIII and IX contain our main results: In Sec. VIII it is shown that the mean values of energy in the thermodynamic approximation are equal for the adiabatic and zero-polytropic processes and in Sec. IX it is shown that the fluctuations for the two cases in general differ from each other. We summarize and discuss our results in Sec. X.

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## II. ZERO-POLYTROPIC PROCESS VERSUS ADIABATIC PROCESS

In the phenomenological description of equilibrium thermodynamic processes, it is always meant that a system possesses a temperature at any moment. A state of the thermodynamic system is then completely determined by the set of external parameters  $a = (a_1, \dots, a_k)$  and the temperature  $T$ ; a process is determined by a function  $T(a)$  [time usually does not figure, but one may add  $a(t)$ , if necessary].

However, arbitrary manipulations with the system can, generally speaking, force it into a state not characterized by temperature. For the system to have a temperature at any moment, one uses a thermostat—a system of much bigger size which is itself in equilibrium and can exchange energy with the system under consideration. The result of an interaction with the thermostat is, on the one hand, that the system receives from it a (positive or negative) amount of energy in the form of heat  $\Delta Q = \int \delta Q$  and, on the other hand, that it is at any moment in a state characterized by the canonical distribution.

Now imagine a process during which the system interacts with the thermostat but

$$\delta Q = 0. \quad (2.1)$$

Since in this case the heat capacity  $c \equiv \frac{\delta Q}{dT} = 0$ , it is natural to call the process *zero polytropic* (recall that a polytropic process is one with constant heat capacity). For a reversible process, Eq. (2.1) is equivalent to

$$dS = 0. \quad (2.2)$$

Knowing the partition function of the system for any  $a$ , one may regard this as a differential equation from which the  $a$  dependence of temperature is to be determined. Given the initial condition  $T|_{a=a_0} = T_0$ , one obtains the equation of zero-polytropic curve

$$T = T_z(a, a_0, T_0). \quad (2.3)$$

On the other hand, a process can be considered which involves no thermostat at all. A system whose interaction with the environment consists only in the change of its external parameters is usually referred to as adiabatically isolated and a process in such a system is called *adiabatic*. For this process (2.1) also takes place, but then the following question arises: Does this imply that *everything* will be the same for adiabatic and zero-polytropic processes, that is, will the adiabatic probability distribution be canonical with the temperature as given by (2.3)?

We know that usually even the question itself is not posed; namely, (2.1) is said to define the adiabatic process and (2.3) is referred to as its equation. But, as mentioned above, since for the adiabatic process the thermostat is actually absent, there is no *a priori* reason to presuppose that the corresponding distribution would be canonical. Therefore the question itself makes sense—and we will see in what follows that in general the answer to it is negative.

## III. THE MICROCANONICAL POSTULATE AND EQUILIBRIUM DISTRIBUTION

A quantum-mechanical system of finite size possesses a countable set of (pure) stationary states. It is customary to arrange those states into energy levels, so the complete set of pure states is  $\{\omega_{ls} : s = 1, \dots, g_l; l = 0, 1, 2, \dots\}$ , where the energy eigenvalues  $\epsilon_l = \omega_{ls}(H)$  do not depend on  $s$  and  $g_l$  is the degeneracy of  $l$ th level. Further, there are mixed states of the form

$$\omega = \sum_{ls} w_{ls} \omega_{ls}, \quad (3.1)$$

where  $w_{ls}$  is the probability of the system being in the state  $\omega_{ls}$ . The probabilities satisfy  $w_{ls} \geq 0$  and the normalization condition

$$\sum_{ls} w_{ls} = 1. \quad (3.2)$$

The mean value of energy in the state (3.1) is

$$E = \sum_{ls} w_{ls} \epsilon_l \quad (3.3)$$

and the entropy is

$$S = - \sum_{ls} w_{ls} \ln w_{ls} \quad (3.4)$$

( $k = 1$ ).

In the case of a time-independent Hamiltonian, in von Neumann dynamics for the statistical operator, any state of the form (3.1) is stationary (that is, it does not change with time). However, for thermodynamic systems the following statement is commonly accepted: Given a fixed energy, that is, if  $w_{ls} \sim \delta_{lL}$ , a “true” stationary—usually called equilibrium—state is only that with  $w_{ls}$  not depending on  $s$  or, taking into account the normalization condition, with

$$w_{ls} = \frac{1}{g_L} \delta_{lL}. \quad (3.5)$$

The distribution (3.5) is known as the microcanonical distribution. The time evolution of a system with fixed energy brings the system eventually to a “microcanonical state” in which (3.5) takes place. Such an evolution is not described by Schrödinger dynamics, but rather by an indeterministic dynamics [1,2]; the statement that the microcanonical state is an equilibrium state is essentially considered a generalization of experimental facts. (Entropy increases during irreversible time evolution and the microcanonical state corresponds to the maximum of entropy for a fixed energy.)

Consider now an arbitrary state of the form (3.1). One can rewrite  $\omega$  as

$$\omega = \sum_l W_l \Omega_l, \quad (3.6)$$

where

$$W_l = \sum_s w_{ls}, \quad (3.7)$$

$$\Omega_l = \sum_s \frac{w_{ls}}{W_l} \omega_{ls}. \quad (3.8)$$

Clearly,  $\Omega_l$  is a state with fixed energy (a mixture of states belonging to the same level,  $w_{ls}/W_l$  being the conditional probabilities) and  $\{W_l\}$  is the distribution over levels. What will be the time evolution of  $\omega$ ? We know already that  $\Omega_l$  evolves into the corresponding microcanonical state; now, conservation of energy means that there can be no transitions between different levels, therefore  $W_l$ 's do not change. In other words, a state (3.1) evolves in such a way that the distribution over levels does not change, but the distribution within each level is equalized. That is, a state of the form (3.1) is an equilibrium state if and only if  $w_{ls'} = w_{ls''}$  takes place for each  $l, s', s''$ . The statement above can be naturally called the *microcanonical postulate* [2]. We stress once more that actually it means nothing but the common statement about a system evolving into a microcanonical state, with the only addition that the exact energy is not known.

For a closed system, an *arbitrary* distribution  $\{W_l\}$  over levels corresponds to an equilibrium state (provided that  $w_{ls'} = w_{ls''}$  takes place). However, there is an important case of a system interacting with a thermostat (recall that the interaction energy is usually neglected). In this case it is known that for the system there will be the canonical distribution, that is,

$$w_{ls} = \exp \left[ \frac{F - \epsilon_l}{T} \right], \quad (3.9)$$

where the free energy  $F$  is determined from the normalization condition and the temperature is  $T = \left( \frac{dS(E)}{dE} \right)^{-1}$  [3], where  $S(E)$  is the entropy of the thermostat in the microcanonical state with energy  $E$ :  $S(E) = \ln G(E)$ ,  $G(E)$  being the degeneracy of the level with energy  $E$ . This distribution corresponds to the maximum of entropy for a given *mean* energy.

Note finally that for a macroscopic system  $g_l$  is a rapidly increasing function of energy (typically like  $\epsilon^{\bar{N}}$ , where  $\bar{N}$  is of the order of number of particles) and therefore for a canonical distribution  $W_l = g_l w_{ls}$  is a sharp-peaked function—similarly to the microcanonical case when it is a  $\delta$  function. This makes the two distributions equivalent in the thermodynamic limit for calculating mean values, but certainly not for fluctuations.

#### IV. ADIABATIC PROCESS AND LEVEL CROSSINGS

It is usually assumed that the Hamiltonian and correspondingly the energy levels depend on the external parameters

$$\epsilon_l = \epsilon_l(a), \quad a = (a_1, \dots, a_k). \quad (4.1)$$

In a process, both  $a$ —and correspondingly  $\epsilon_l$ —and the probabilities  $w_l$  change. For a given quasistatic process the probabilities “follow” the external parameters, so there are the dependences  $w_l(a)$ . To calculate these, one has, generally speaking, to solve the dynamical equa-

tions taking into account the behavior of the system itself and its interaction with the environment, which is surely impossible for a macroscopic system. If, however, a thermostat is present (as it is for a zero-polytropic process), then as a result of the interaction with it the distribution is canonical at every moment,

$$w_l^{(c)}(a) = \exp \left[ \frac{F(a) - \epsilon_l(a)}{T(a)} \right], \quad (4.2)$$

where  $T(a)$  is a given function which is fixed by the thermostat.

Now assume that the initial distribution is canonical,

$$w_l(a_0) = \exp \left[ \frac{F_0 - \epsilon_l(a_0)}{T_0} \right], \quad (4.3)$$

and a quasistatic adiabatic process (in the thermodynamic sense) is carried out. If there are no level crossings, then the quantum-mechanical adiabatic theorem [4] holds and one has

$$w_l^{(\text{ad})}(a) = w_l(a_0) \quad (4.4)$$

(transitions between levels are absent). The question is: Does  $w_l^{(\text{ad})}(a) = w_l^{(c)}(a)$  take place? By comparing (4.2) and (4.3) it is easy to see that it does if and only if one can write  $\epsilon_l(a)$  as

$$\epsilon_l(a) = \xi_l \lambda(a) + \nu(a) \quad (4.5)$$

for all  $l$ ; substituting this and

$$T(a) = T_0 \frac{\lambda(a)}{\lambda(a_0)}, \quad F(a) = [F_0 - \nu(a_0)] \frac{\lambda(a)}{\lambda(a_0)} + \nu(a) \quad (4.6)$$

into (4.2) leads just to (4.3). Actually,  $T(a)$  here will be the same as in (2.3) for the zero-polytropic curve. Thus, for the adiabatic distribution to be canonical—and for the adiabatic curve to coincide with the zero-polytropic one—the  $a$  dependences of  $\epsilon_l$  have to be rather strongly correlated ( $l$  figures only in the  $a$  independent  $\xi_l$ 's); in essence, only shifting and extending (squeezing) the spectrum as a whole is allowed. Clearly, for an arbitrary set of functions  $\epsilon_l(a)$  one cannot satisfy an infinite number of equations (4.5) at any  $a$  by choosing only two values  $\lambda(a)$  and  $\nu(a)$ ; thus  $w_l^{(\text{ad})}(a)$  in general differ from  $w_l^{(c)}(a)$ .

A special consideration is required if level crossings occur for some  $a = a_{\text{cr}}$ , that is, if

$$\epsilon_{l'}(a_{\text{cr}}) = \epsilon_{l''}(a_{\text{cr}}), \quad l' \neq l''. \quad (4.7)$$

Note that in this case Eq. (4.5) certainly cannot be fulfilled because together with (4.7) it would imply  $\epsilon_{l'}(a) = \epsilon_{l''}(a)$  for all  $a$ , which means  $l'$  and  $l''$  refer to the same level. Before the crossing, the values  $w_{l'}(a_{\text{cr}} - 0)$  and  $w_{l''}(a_{\text{cr}} - 0)$  would in general be different. But the microcanonical postulate, once accepted, tells us that at the moment of crossing the probabilities for all the states belonging to the levels  $l'$  and  $l''$  should become equal. This implies that after the crossing one will have

$$\begin{aligned} w_{l'}(a_{\text{cr}} + 0) &= w_{l''}(a_{\text{cr}} + 0) \\ &= \frac{g_{l'} w_{l'}(a_{\text{cr}} - 0) + g_{l''} w_{l''}(a_{\text{cr}} - 0)}{g_{l'} + g_{l''}}. \end{aligned} \quad (4.8)$$

Thus in an adiabatic process the probability corresponding to a certain level remains constant so far as there are no crossings, but changes according to (4.8) at a crossing. Note that in fact two conditions of slowness are implicated here: First, the process has to be slow enough for the adiabatic theorem to be applicable and second, enough time has to be provided for the equalization as in (4.8) to accomplish. The latter means that due to a small interaction with the environment, which, strictly speaking, is always present, the levels have a small but finite width and, on the other hand, equalization occurs not at the mathematical point of level crossing, but in its small vicinity; so the process should be slow enough for the time when  $\epsilon_{l'}(a)$  and  $\epsilon_{l''}(a)$  are close enough to exceed the time of equalizing. In what follows we will make no estimates of speed, but just assume that the process is slow enough to meet both conditions.

We conclude from what has been said so far that the adiabatic process in general *differs* from the zero-polytropic process. Furthermore, it is clear from (4.8) that whenever  $w_{l'}(a_{\text{cr}} - 0) \neq w_{l''}(a_{\text{cr}} - 0)$ , there is an entropy increase at the crossing (while in a zero-polytropic process entropy is constant by definition). Any other specific conclusions demand additional information on the functions  $\epsilon_l(a)$ .

## V. QUASICONTINUOUS SPECTRUM: THE WAVE EQUATION

When considering thermodynamic systems it is usually safe to assume that level spacing is small enough so that summation over levels may be replaced by integration. This is the essence of the quasicontinuous spectrum approximation. (It should be stressed that the spectrum is *discrete* and the wave functions are normalizable; in fact, we only introduce a more convenient way of counting.) Instead of  $g_l$ 's, the density of states  $G(\epsilon, a)$  is introduced, which is a continuous function such that  $G(\epsilon, a)\Delta\epsilon$  is the number of states whose energy is in a narrow interval  $[\epsilon - \Delta\epsilon/2, \epsilon + \Delta\epsilon/2]$ . The probability distribution is characterized by a function  $w(\epsilon, a)$ ,  $w$  being the probability of the system being in a pure state with energy  $\epsilon$  (but not the probability density). The equalities (3.2)–(3.4) become

$$\int_0^\infty G(\epsilon, a) w(\epsilon, a) d\epsilon = 1, \quad (5.1)$$

$$E = \int_0^\infty G(\epsilon, a) w(\epsilon, a) \epsilon d\epsilon, \quad (5.2)$$

$$S = - \int_0^\infty G(\epsilon, a) w(\epsilon, a) \ln w(\epsilon, a) d\epsilon. \quad (5.3)$$

We will now derive the equation that, for an adiabatic process, is satisfied by  $w(\epsilon, a)$ . In a discrete spectrum, there is still the set of functions  $\epsilon_l(a)$ . Consider an infinitesimal interval  $[\epsilon - \Delta\epsilon/2, \epsilon + \Delta\epsilon/2]$ . It contains

$G(\epsilon, a)\Delta\epsilon$  states in total; let  $\mathcal{L}(\epsilon, \Delta\epsilon, a) = \{l : \epsilon_l(a) \in [\epsilon - \Delta\epsilon/2, \epsilon + \Delta\epsilon/2]\}$  be the set of numbers of relevant levels. The probability for the system to occupy one of these states is  $w(\epsilon, a)$ . Now, at a previous moment the energy of the  $l$ th level was  $\epsilon_l(a - da) = \epsilon_l(a) - v_l(a)da$ , where  $v_l(a) = d\epsilon_l(a)/da$ , and the corresponding probability was  $w(\epsilon - v_l(a)da, a - da)$ . In the spirit of (4.8) one gets

$$w(\epsilon, a) = \frac{\sum_{l \in \mathcal{L}(\epsilon, \Delta\epsilon, a)} g_l w(\epsilon - v_l(a)da, a - da)}{\sum_{l \in \mathcal{L}(\epsilon, \Delta\epsilon, a)} g_l}. \quad (5.4)$$

Expanding  $w$  in the numerator and taking into account that the denominator is  $G(\epsilon, a)\Delta\epsilon$ , one comes to the equation

$$\frac{\partial w(\epsilon, a)}{\partial a} = u(\epsilon, a) \frac{\partial w(\epsilon, a)}{\partial \epsilon} \quad (5.5)$$

where

$$u(\epsilon, a) = - \frac{1}{G(\epsilon, a)\Delta\epsilon} \sum_{l \in \mathcal{L}(\epsilon, \Delta\epsilon, a)} g_l v_l(a). \quad (5.6)$$

An equation of the form (5.5) is known as a wave equation and  $u(\epsilon, a)$  is called the wave velocity. Equation (5.6) can be used to determine the wave velocity if the whole set of functions  $\epsilon_l(a)$  is known. (Clearly, the sum on the right-hand side will be proportional to  $\Delta\epsilon$  for sufficiently small  $\Delta\epsilon$ .) However, in the quasicontinuous spectrum approximation it is sufficient to know just  $G(\epsilon, a)$ . Indeed, let us introduce the quantity  $\mathcal{G}(\epsilon, a) \equiv \int_0^\epsilon G(\epsilon', a) d\epsilon'$ , which is the number of states whose energy does not exceed  $\epsilon$ . Let there be some value  $v$  and consider those levels for which  $v_l(a) = v$ . As  $a$  changes by  $da$ , the states whose energy belongs to the interval  $[\epsilon - v da, \epsilon]$  leave (if  $v > 0$ ) or enter (if  $v < 0$ ) the interval  $[0, \epsilon]$ ; the quantity of such states may be written as  $\frac{|v da|}{\Delta\epsilon} \sum_{\substack{l \in \mathcal{L}(\epsilon, \Delta\epsilon, a) \\ v_l(a) = v}} g_l$  (the sum is the quantity of states in the interval of width  $\Delta\epsilon$ , hence the prefactor). Thus the change in  $\mathcal{G}(\epsilon, a)$  equals  $-\frac{1}{\Delta\epsilon} \sum_{\substack{l \in \mathcal{L}(\epsilon, \Delta\epsilon, a) \\ v_l(a) = v}} g_l v da$ . To obtain the total change of  $\mathcal{G}(\epsilon, a)$  one should sum over all possible values of  $v$ ; thus  $\frac{\partial \mathcal{G}(\epsilon, a)}{\partial a} = -\frac{1}{\Delta\epsilon} \sum_{l \in \mathcal{L}(\epsilon, \Delta\epsilon, a)} g_l v_l(a)$  and consequently

$$u(\epsilon, a) = \frac{1}{G(\epsilon, a)} \int_0^\epsilon \frac{\partial G(\epsilon', a)}{\partial a} d\epsilon'. \quad (5.7)$$

Note that if it is *given* that  $w(\epsilon, a)$  obeys the wave equation with a velocity that does not depend on  $w(\epsilon, a)$  itself, then the expression (5.7) follows directly from the normalization condition. Indeed, differentiating (5.1) with respect to  $a$  and substituting  $\frac{\partial w(\epsilon, a)}{\partial a}$  from (5.5) yields

$$\begin{aligned} \int_0^\infty \frac{\partial G(\epsilon, a)}{\partial a} w(\epsilon, a) d\epsilon \\ + \int_0^\infty G(\epsilon, a) u(\epsilon, a) \frac{\partial w(\epsilon, a)}{\partial \epsilon} d\epsilon = 0 \end{aligned} \quad (5.8)$$

or

$$\int_0^\infty \left\{ \frac{\partial G(\epsilon, a)}{\partial a} - \frac{\partial}{\partial \epsilon} [G(\epsilon, a)u(\epsilon, a)] \right\} w(\epsilon, a) d\epsilon = 0. \quad (5.9)$$

Since the previous consideration of the adiabatic process allows  $w(\epsilon, a)$  to be arbitrary, it follows that

$$\frac{\partial G(\epsilon, a)}{\partial a} = \frac{\partial}{\partial \epsilon} [G(\epsilon, a)u(\epsilon, a)]; \quad (5.10)$$

this immediately implies (5.7).

Finally, note that if  $\varphi(x)$  is an arbitrary differentiable function and  $w(\epsilon, a)$  is a solution of the wave equation, then  $\varphi(w(\epsilon, a))$  is also a solution. Therefore the quantity

$$\Phi(a) = \int_0^\infty G(\epsilon, a)\varphi(w(\epsilon, a)) d\epsilon \quad (5.11)$$

does not depend on  $a$ , i.e.,  $d\Phi/da = 0$ , by the same reason as for the normalization integral (5.1). In particular, choosing  $\varphi(x) = -x \ln x$  yields

$$\frac{dS}{da} = 0; \quad (5.12)$$

entropy is conserved for an adiabatic process in the quasicontinuous spectrum approximation. This does not of course contradict what has been said earlier. Briefly, it means that if one considers the level spacing to be an infinitesimal quantity of the first order, then the probabilities corresponding to the two levels before a crossing differ in the first order and therefore the entropy increase at the crossing is of the second order (because the uniform distribution corresponds to the maximum of entropy and the change of a function near a maximum is of the second order with respect to the change of its argument). The total entropy increase then tends to zero together with the level spacing.

## VI. SOLUTION OF THE WAVE EQUATION

The wave equation is solved by the standard method of characteristics [5]. Namely, consider an auxiliary differential equation

$$\frac{d\epsilon}{da} = -u(\epsilon, a). \quad (6.1)$$

Its solutions form a family of curves in the  $(a, \epsilon)$  plane, which are called characteristics of the equation (5.5). Let us write down the equation of these curves as  $\epsilon = \chi(\epsilon_0, a_0, a)$ , where  $(a_0, \epsilon_0)$  is an "initial point" of the curve. Since it does not matter which point is chosen as initial, one has as well  $\epsilon_0 = \chi(\epsilon, a, a_0)$ . Then the general solution of (5.5) is

$$w(\epsilon, a) = f(\chi(\epsilon, a, a_0)) \quad (6.2)$$

with arbitrary  $a_0$  and  $f$ . If an initial distribution is given

$$w(\epsilon, a)|_{a=a_0} = w_0(\epsilon), \quad (6.3)$$

then the corresponding particular solution is

$$w(\epsilon, a) = w_0(\chi(\epsilon, a, a_0)); \quad (6.4)$$

it satisfies (6.3) because  $\chi(\epsilon, a_0, a_0) = \epsilon$ .

Any solution of the form (6.2) remains constant when the point  $(a, \epsilon)$  moves along a characteristic—this is, in fact, another definition of the latter. If there are no level crossings, the characteristics are nothing but the functions  $\epsilon_l(a)$  for all the levels; so the probability is constant for each level. If, however, level crossings are present, this is certainly not the case.

## VII. CANONICAL SYSTEMS

It has been established that the distribution corresponding to an adiabatic process is obtained by solving the wave equation. We turn now to our original question: Under what condition is this distribution canonical? So far we only know that in one particular case it is and in general it is not. Let there be an initial canonical distribution

$$w_0(\epsilon) = \exp \left[ \frac{F_0 - \epsilon}{T_0} \right]; \quad (7.1)$$

then the two processes starting from it yield the two distributions:  $w(\epsilon, a)$  defined by (6.4) for the adiabatic process and

$$w_z(\epsilon, a) = \exp \left[ \frac{F - \epsilon}{T} \right] \quad (7.2)$$

for the zero-polytropic process. Here  $T = T_z(a, a_0, T_0)$  as in (2.3). The question is: When does

$$w(\epsilon, a) = w_z(\epsilon, a) \quad (7.3)$$

take place?

Let us define the "zero-polytropic velocity" by the equality analogous to the wave equation

$$\frac{\partial w_z(\epsilon, a)}{\partial a} = u_z \frac{\partial w_z(\epsilon, a)}{\partial \epsilon}. \quad (7.4)$$

It follows from the aforesaid that  $u_z$ , unlike  $u$ , in general depends on the initial condition  $u_z = u_z(\epsilon, a, a_0, T_0)$ . We will now prove that Eq. (7.3) takes place if and only if

$$\frac{\partial u_z(\epsilon, a, a_0, T_0)}{\partial T_0} = 0. \quad (7.5)$$

*Proof.* First note that Eq. (7.3) is equivalent to

$$u(\epsilon, a) = u_z(\epsilon, a, a_0, T_0). \quad (7.6)$$

Since there is the equation (5.5) for  $w(\epsilon, a)$  and the equality (7.4) for  $w_z(\epsilon, a)$  and the initial condition (7.1) is the same for both, (7.6) implies (7.3). Since  $u = \frac{\partial w}{\partial a} / \frac{\partial w}{\partial \epsilon}$  and the same for  $u_z$  and  $w_z$ , (7.3) implies (7.6).

Now, if (7.5) is *not* fulfilled, (7.6) and therefore (7.3)

cannot be true. On the other hand, let (7.5) be fulfilled. First we will show that in this case

$$\frac{\partial u_z(\epsilon, a, a_0, T_0)}{\partial a_0} = 0 \quad (7.7)$$

also holds. Indeed, the two points  $(a_0, T_0)$  and  $(a, T_z(a, a_0, T_0))$  in the  $(a, T)$  plane belong to the same zero-polytropic curve and it does not matter which one of them is considered initial. Hence

$$u_z(\epsilon, a, a_0, T_0) = u_z(\epsilon, a, a, T_z(a, a_0, T_0)), \quad (7.8)$$

from which (7.7) immediately follows upon differentiating with respect to  $a_0$  and using (7.5). So one can write  $u_z(\epsilon, a, a_0, T_0) = u_z(\epsilon, a)$ . Further, there is the equality (5.8) for  $w(\epsilon, a)$  and the analogous one, with  $u(\epsilon, a)$  replaced by  $u_z(\epsilon, a)$ , for  $w_z(\epsilon, a)$ . At  $a = a_0$  the first terms on the left-hand sides of both equations coincide and one can equate the second terms; taking into account the initial condition (7.1), one gets

$$\int_0^\infty \exp\left[-\frac{\epsilon}{T_0}\right] G(\epsilon, a_0) [u(\epsilon, a_0) - u_z(\epsilon, a_0)] = 0. \quad (7.9)$$

The left-hand side is the Laplace transform of the function  $G(\epsilon, a_0) [u(\epsilon, a_0) - u_z(\epsilon, a_0)]$  with respect to  $\epsilon$ ; since  $T_0$  may be chosen at will, the function itself must vanish. Formally replacing  $a_0$  (which is also arbitrary) by  $a$ , one has  $u(\epsilon, a) = u_z(\epsilon, a)$ . Q.E.D.

One now derives the explicit expression for  $u_z$  in order to see when it does not depend on  $T_0$ . Equation (7.2) can be rewritten as

$$w_z(\epsilon, a) = \exp\left[-S + \frac{E - \epsilon}{T}\right], \quad (7.10)$$

where  $E = E(a, T)$  is the mean energy and the entropy  $S = \text{const}$ . Therefore

$$\begin{aligned} \frac{\partial w_z(\epsilon, a)}{\partial \epsilon} &= -\frac{w_z(\epsilon, a)}{T}, \quad (7.11) \\ \frac{\partial w_z(\epsilon, a)}{\partial a} &= w_z(\epsilon, a) \frac{\partial}{\partial a} \left( \frac{E - \epsilon}{T} \right) \\ &= w_z(\epsilon, a) \frac{\left( \frac{\partial E}{\partial a} + \frac{\partial E}{\partial T} \frac{dT}{da} \right) T - \frac{dT}{da} (E - \epsilon)}{T^2}, \end{aligned} \quad (7.12)$$

and

$$u_z(\epsilon, a, a_0, T_0) = \frac{dT}{da} \left( \frac{E - \epsilon}{T} - \frac{\partial E}{\partial T} \right) - \frac{\partial E}{\partial a} \quad (7.13)$$

[recall that  $T = T_z(a, a_0, T_0)$  is meant here].

Let us call a system "canonical" if (7.5) is fulfilled for it. In a canonical system, an adiabatic process starting from a canonical distribution will completely coincide with the corresponding zero-polytropic process, despite the absence of a thermostat in one case and its presence in the other one. We already know one example of a canonical system—the one for which (4.5) is fulfilled; to verify (7.5) in this case is a matter of straightforward calculation. Another important example is a system with

$$E(a, T) = cT + \zeta(a), \quad (7.14)$$

which holds in the classical limit for a system with quadratic degrees of freedom, when the theorem of uniform distribution of energy over degrees of freedom takes place, with the possible addition of the static energy of interaction (as in the van der Waals gas). Indeed, since the mean energy is expressed in terms of the partition function as  $E = T^2 \frac{\partial \ln Z}{\partial T}$ , (7.14) implies

$$\ln Z = c \ln T - \frac{\zeta(a)}{T} - c\Psi(a), \quad (7.15)$$

where  $\Psi(a)$  is a function determined independently of  $c$  and  $\zeta(a)$ . Then

$$S = \frac{\partial}{\partial T} (T \ln Z) = c(\ln T - \Psi(a) + 1) \quad (7.16)$$

and the equation of zero-polytropic process  $S = \text{const}$  implies

$$T_z(a, a_0, T_0) = T_0 \exp[\Psi(a) - \Psi(a_0)]; \quad (7.17)$$

substituting this and (7.14) into (7.13) yields

$$u_z(\epsilon, a, T_0, a_0) = [\zeta(a) - \epsilon] \frac{d\Psi}{da} - \frac{d\zeta}{da}, \quad (7.18)$$

which indeed does not depend on  $T_0$ . Thus a system for which (7.14) takes place is canonical—the adiabatic and zero-polytropic processes coincide for it.

### VIII. THE THERMODYNAMIC LIMIT: COINCIDENCE OF THE ADIABATIC AND ZERO-POLYTROPIC PROCESSES

The probability distribution determines the values of all thermodynamic quantities. In general the distributions and the mean values are different for adiabatic and zero-polytropic processes. However, we will now show that in the thermodynamic limit the mean values of energy coincide. In this limit one has  $E \sim N$ , where  $N$  is the number of particles and  $\frac{1}{N}$  is small; what we will show is that the difference between the two mean values is small in the same sense.

For a macroscopic system  $G(\epsilon, a)$  is a rapidly increasing function (typically like  $\epsilon^N$  with  $\bar{N} \sim N$ ); this means that  $G(\epsilon, a)w_z(\epsilon, a)$  is a sharp-peaked function of  $\epsilon$  for any fixed  $a$ . One has then, to an accuracy of  $\frac{1}{N}$ ,

$$\int_0^\infty G(\epsilon, a)w_z(\epsilon, a)f(\epsilon, a) d\epsilon \simeq f(E(a, T), a) \quad (8.1)$$

for any "sufficiently smooth" function  $f$ , since in this approximation the point of maximum of  $G(\epsilon, a)w_z(\epsilon, a)$  is the mean value  $E(a, T)$ . Let  $f(\epsilon, a) = u(\epsilon, a)$ . Writing

$$w_z(\epsilon, a) = \frac{1}{Z(a, T)} \exp\left[-\frac{\epsilon}{T}\right], \quad (8.2)$$

where  $Z(a, T) = \int_0^\infty G(\epsilon, a) \exp\left[-\frac{\epsilon}{T}\right] d\epsilon = \exp\left[-\frac{F(a, T)}{T}\right]$ , one has

$$\begin{aligned}
\int_0^\infty G(\epsilon, a) w_z(\epsilon, a) u(\epsilon, a) d\epsilon &= \frac{1}{Z(a, T)} \int_0^\infty d\epsilon \exp\left[-\frac{\epsilon}{T}\right] \frac{\partial}{\partial a} \int_0^\epsilon G(\epsilon', a) d\epsilon' \\
&= -\frac{T}{Z(a, T)} \frac{\partial}{\partial a} \int_0^\infty d\epsilon \frac{d}{d\epsilon} \left( \exp\left[-\frac{\epsilon}{T}\right] \right) \int_0^\epsilon G(\epsilon', a) d\epsilon' \\
&= \frac{T}{Z(a, T)} \frac{\partial}{\partial a} \int_0^\infty d\epsilon \exp\left[-\frac{\epsilon}{T}\right] G(\epsilon, a) = \frac{T}{Z(a, T)} \frac{\partial Z(a, T)}{\partial a} \\
&= -\frac{\partial F(a, T)}{\partial a}.
\end{aligned} \tag{8.3}$$

This is an exact result. A comparison with (8.1) yields

$$u(E(a, T), a) \simeq -\frac{\partial F(a, T)}{\partial a}. \tag{8.4}$$

More accurately, denoting  $W_z(\epsilon, a) \equiv G(\epsilon, a)w_z(\epsilon, a)$ , writing

$$W_z(\epsilon, a) \simeq W_z(E, a) \exp\left[-\frac{(\epsilon - E)^2}{2\kappa_z^2}\right], \tag{8.5}$$

where  $E$  stands for  $E(a, T)$ , and expanding  $u(\epsilon, a)$  around  $\epsilon = E$ , one has

$$\begin{aligned}
\int_0^\infty W_z(\epsilon, a) u(\epsilon, a) d\epsilon &\simeq W_z(E, a) \left[ u(E, a) \int_0^\infty \exp\left[-\frac{(\epsilon - E)^2}{2\kappa_z^2}\right] d\epsilon + \frac{1}{2} \frac{\partial^2 u(E, a)}{\partial E^2} \int_0^\infty (\epsilon - E)^2 \exp\left[-\frac{(\epsilon - E)^2}{2\kappa_z^2}\right] d\epsilon \right] \\
&= u(E, a) + \frac{\kappa_z^2}{2} \frac{\partial^2 u(E, a)}{\partial E^2} \\
&= u(E, a) - \frac{1}{2} \frac{W_z(E, a)}{\partial^2 W_z(E, a)} \frac{\partial^2 u(E, a)}{\partial E^2}.
\end{aligned} \tag{8.6}$$

Considering  $W_z$  to be a sharp enough function of  $\epsilon$  means that  $\kappa$  is small enough, that is,  $\frac{\partial^2 W_z(E, a)}{\partial E^2} / W_z(E, a)$  is large enough so that one can neglect the second term to get (8.4). Since  $\kappa$  is the mean square fluctuation of energy, the approximation under consideration, in essence, means that the fluctuation is small compared to the mean value.

Now let us derive the equation for the mean energy in an adiabatic process. We expect that in the thermodynamic limit,  $W(\epsilon, a) \equiv G(\epsilon, a)w(\epsilon, a)$  also has to be a sharp-peaked function (this will be justified later as we will see the fluctuation to be of the same order as for the zero-polytropic process). Then the mean value  $E_{\text{ad}}(a)$  is to be determined from the equation

$$R(E_{\text{ad}}, a) = 0, \tag{8.7}$$

where by definition

$$R(\epsilon, a) = \frac{\partial W(\epsilon, a)}{\partial \epsilon}. \tag{8.8}$$

It follows from (8.7) that

$$\frac{dE_{\text{ad}}}{da} = v(E_{\text{ad}}, a), \tag{8.9}$$

where

$$v(\epsilon, a) = -\frac{\partial R(\epsilon, a)}{\partial a} \Big/ \frac{\partial R(\epsilon, a)}{\partial \epsilon}. \tag{8.10}$$

Substituting (8.8) and using (5.5) and (5.10) to replace derivatives with respect to  $a$  by derivatives with respect

to  $\epsilon$ , we come to

$$v(E_{\text{ad}}, a) = -u(E_{\text{ad}}, a) - \frac{W(E_{\text{ad}}, a)}{\frac{\partial^2 W(E_{\text{ad}}, a)}{\partial E_{\text{ad}}^2}} \frac{\partial^2 u(E_{\text{ad}}, a)}{\partial E_{\text{ad}}^2}. \tag{8.11}$$

The second term, being of the same form as in (8.6), may again be neglected, producing a relative error of the order  $\frac{1}{N}$ . Now (8.4) may be rewritten as

$$u(\epsilon, a) \simeq -\frac{\partial F(a, T)}{\partial a} \Big|_{T=T(\epsilon, a)}, \tag{8.12}$$

where  $T = T(\epsilon, a)$  is the solution of the equation  $E(a, T) = \epsilon$ . Equation (8.9) becomes then

$$\frac{dE_{\text{ad}}}{da} \simeq \frac{\partial F(a, T)}{\partial a} \Big|_{T=T(E_{\text{ad}}, a)}. \tag{8.13}$$

We recognize here the equation for the mean energy for a zero-polytropic process (usually referred to as an adiabatic process), which follows from the second law of thermodynamics upon setting  $dS = 0$ . Thus, in the thermodynamic limit the mean values of energy for the adiabatic and zero-polytropic processes coincide. That is, if the initial distribution for both is (7.1), then

$$E_{\text{ad}}(a) \simeq E(a, T), \tag{8.14}$$

where

$$T = T_z(a, a_0, T_0). \tag{8.15}$$

### IX. GAUSSIAN APPROXIMATION AND FLUCTUATIONS

The essence of the Gaussian approximation is as follows: The density of states  $G(\epsilon, a)$  being a rapidly increasing function of  $\epsilon$ , we assume that for all probability distributions  $w(\epsilon, a)$  involved, the above-introduced function  $W(\epsilon, a) \equiv G(\epsilon, a)w(\epsilon, a)$ , which always has a maximum at some point  $E$ , can be represented with sufficient precision as

$$W(\epsilon, a) = W(E, a) \exp \left[ -\frac{(\epsilon - E)^2}{2\kappa^2} \right]. \quad (9.1)$$

In this approximation the mean value of energy is  $\langle \epsilon \rangle = E$  and the mean square deviation (fluctuation) is

$$\Delta E = \sqrt{\langle \epsilon^2 \rangle - E^2} = \kappa. \quad (9.2)$$

One now calculates  $\kappa$  for an adiabatic process in order to compare it with the known value for a zero-polytropic one. However, before proceeding let us note the following point. It follows from the definition of entropy that

$$S = - \int_0^\infty W(\epsilon, a) \ln W(\epsilon, a) d\epsilon + \int_0^\infty W(\epsilon, a) \ln G(\epsilon, a) d\epsilon; \quad (9.3)$$

accepting (9.1) and assuming  $G(\epsilon, a) \sim \epsilon^N$ , one has

$$S \simeq \ln \frac{\kappa}{e_1} + N \ln \frac{E}{e_0}, \quad (9.4)$$

where  $e_0$  and  $e_1$  are values (in general,  $a$  dependent) of dimensionality of energy. The value of entropy for any given  $a$  is the same for the adiabatic and zero-polytropic processes. If the corresponding mean values of energy are *exactly* equal, as for a canonical system, then, according to (9.4), the fluctuations also coincide. But if the relative difference between the two values is of the order  $\frac{1}{N}$ , as shown in Sec. VIII, then to compensate for it a relative difference in  $\kappa$  of the order of unity is needed, as (9.4) shows. We conclude that in general the difference between energy fluctuations for adiabatic and zero-polytropic processes should be of the same order as those fluctuations themselves, i.e., quite significant.

We turn now to the explicit calculation. Let us write the adiabatic distribution as

$$w(\epsilon, a) = \exp[-\gamma(\epsilon, a)] \quad (9.5)$$

(considering this as the definition of  $\gamma$ ) and expand  $\gamma(\epsilon, a)$  in a point  $\tilde{E}$ , which we do not fix for the time being:

$$\gamma(\epsilon, a) \simeq \gamma(\tilde{E}, a) + \frac{\epsilon - \tilde{E}}{\tilde{T}} + \frac{1}{2} \left( \frac{\partial^2 \gamma}{\partial \epsilon^2} \right) \Big|_{\epsilon=\tilde{E}} (\epsilon - \tilde{E})^2, \quad (9.6)$$

where by definition

$$\frac{1}{\tilde{T}} = \left( \frac{\partial \gamma}{\partial \epsilon} \right) \Big|_{\epsilon=\tilde{E}}. \quad (9.7)$$

One then has

$$W(\epsilon, a) = G(\epsilon, a) \exp \left[ -\frac{\epsilon}{\tilde{T}} \right] \exp \left[ -\gamma(\tilde{E}, a) + \frac{\tilde{E}}{\tilde{T}} - \frac{1}{2} \left( \frac{\partial^2 \gamma}{\partial \epsilon^2} \right) \Big|_{\epsilon=\tilde{E}} (\epsilon - \tilde{E})^2 \right]. \quad (9.8)$$

For the first two factors the Gaussian approximation can be used again,

$$G(\epsilon, a) \exp \left[ -\frac{\epsilon}{\tilde{T}} \right] = G(E(a, \tilde{T}), a) \exp \left[ -\frac{E(a, \tilde{T})}{\tilde{T}} \right] \times \exp \left[ -\frac{[\epsilon - E(a, \tilde{T})]^2}{2\kappa^2(a, \tilde{T})} \right], \quad (9.9)$$

where  $E(a, \tilde{T})$  is the mean energy in the canonical state with temperature  $\tilde{T}$  and

$$\kappa(a, \tilde{T}) = \sqrt{c_a(a, \tilde{T})\tilde{T}} \quad (9.10)$$

is the relevant fluctuation [ $c_a(a, \tilde{T}) = \frac{\partial E(a, \tilde{T})}{\partial \tilde{T}}$  is the heat capacity at constant  $a$ ] [3]. Substituting (9.9) in (9.8), one sees that if

$$\tilde{E} = E(a, \tilde{T}), \quad (9.11)$$

then (9.8) transforms into

$$W(\epsilon, a) = W(\tilde{E}, a) \exp \left\{ -\frac{1}{2} \left[ \frac{1}{\kappa^2(a, \tilde{T})} + \left( \frac{\partial^2 \gamma}{\partial \epsilon^2} \right) \Big|_{\epsilon=\tilde{E}} \right] (\epsilon - \tilde{E})^2 \right\}, \quad (9.12)$$

so that  $\tilde{E}$  is the maximum point of  $W(\epsilon, a)$ ,  $\tilde{E} = E_{\text{ad}}(a)$ , and the fluctuation in the adiabatic process is found to be

$$\kappa_{\text{ad}} = \left[ \frac{1}{\kappa^2(a, \tilde{T})} + \left( \frac{\partial^2 \gamma}{\partial \epsilon^2} \right) \Big|_{\epsilon=\tilde{E}} \right]^{-1/2}. \quad (9.13)$$

For a given  $G(\epsilon, a)$  one should calculate  $E(a, T)$ , find  $\gamma(\epsilon, a)$  by solving the wave equation, and then there are two equations (9.7) and (9.11) from which  $\tilde{E}$  and  $\tilde{T}$  should be determined, to be substituted in (9.13). On the other hand, we have learned that  $\tilde{E} \simeq E(a, T_z(a, a_0, T_0))$ ; this means in turn that  $\tilde{T} \simeq T_z(a, a_0, T_0)$ , hence the fluctuation in the zero-polytropic process is just

$$\kappa_z = \kappa(a, \tilde{T}). \quad (9.14)$$

Substituting the above-given approximate values of  $\tilde{E}$  and  $\tilde{T}$  in the last two formulas is certainly allowable as it will produce a relative error still of the order  $\frac{1}{N}$  and not 1 as it would be with (9.4).

To compare  $\kappa_{\text{ad}}$  with  $\kappa_z$  one has to calculate the second derivative in (9.13). As before, let us assume the initial distribution to be of the form (7.1); it follows then from



(9.5) and (6.4) that

$$\left. \left( \frac{\partial^2 \gamma}{\partial \epsilon^2} \right) \right|_{\epsilon=\bar{E}} = \frac{1}{T_0} \left. \left( \frac{\partial^2 \chi(\epsilon, a, a_0)}{\partial \epsilon^2} \right) \right|_{\epsilon=\bar{E}}. \quad (9.15)$$

Further, the results of Sec. VIII tell us that  $\chi$  is essentially the dependence  $E(a)$  for the zero-polytropic curve. In other words, if

$$\epsilon = E(a, \theta), \quad \epsilon_0 = E(a_0, \theta_0), \quad \theta = T_z(a, a_0, \theta_0), \quad (9.16)$$

then  $\chi(\epsilon, a, a_0) = \epsilon_0$ . Changing  $\epsilon_0$  by  $d\epsilon_0$  means changing the entropy by  $dS_0 = \frac{d\epsilon_0}{\theta_0}$ . Since entropy is conserved in a zero-polytropic process, this will change  $\epsilon$  in such a way that  $dS = \frac{d\epsilon}{\theta} = dS_0$ ; hence  $\frac{\partial \chi(\epsilon, a, a_0)}{\partial \epsilon} = \frac{\theta_0}{\theta}$  and

$$\begin{aligned} \frac{\partial^2 \chi(\epsilon, a, a_0)}{\partial \epsilon^2} &= \frac{\frac{\partial \theta_0}{\partial \epsilon} \theta - \frac{\partial \theta}{\partial \epsilon} \theta_0}{\theta^2} = \frac{\frac{\partial \theta_0}{\partial \epsilon_0} \frac{d\epsilon_0}{d\epsilon} \theta - \frac{\partial \theta}{\partial \epsilon} \theta_0}{\theta^2} \\ &= \frac{\theta_0}{\theta^2} \left( \frac{\partial \theta_0}{\partial \epsilon_0} - \frac{\partial \theta}{\partial \epsilon} \right) \\ &= \frac{\theta_0}{\theta^2} \left( \frac{1}{c_a(a_0, \theta_0)} - \frac{1}{c_a(a, \theta)} \right). \end{aligned} \quad (9.17)$$

In our case  $\theta = \tilde{T}$ ,  $\theta_0 = T_0$ , and substituting (9.17) in (9.15) and then in (9.13) finally yields

$$\kappa_{\text{ad}} = \sqrt{c_a(a_0, T_0)} \tilde{T}. \quad (9.18)$$

This is the second main result of the present paper, together with (8.14).

If (7.14) is fulfilled, then  $c_a(a, T) = c$  is a constant, and (9.10) and (9.18) give the same result, which reflects the fact that adiabatic and zero-polytropic processes coincide in this case. But whenever  $c_a$  is  $a$  and/or  $T$  dependent, the fluctuations of energy for the two processes are different from each other.

## X. SUMMARY AND DISCUSSION

We would like now to recall briefly our argumentation and principal results. Our starting point was the statement that in an adiabatic process, when there is no thermostat, there is no reason to presuppose that the probability distribution would be canonical, as is implied in the existing phenomenological theory. Instead, what is in fact considered in that theory is a zero-polytropic process, that is, a polytropic process with zero heat capacity. The main question that we are addressing in this paper is whether the probability distributions coincide for adiabatic and zero-polytropic processes. In considering this, the first point is to find the law that the adiabatic distribution obeys. We accept the microcanonical postulate—the statement according to which a system left by itself comes into an equilibrium state, in which the probability of its being in a pure state depends only on the energy of the latter. One then gets the following picture for an adi-

atic process: The probability corresponding to a certain level is constant so far as there are no level crossings, while probabilities equalize at a crossing. This equalization, generally speaking, leads to an entropy increase, so that an adiabatic process would not coincide with the corresponding zero-polytropic one (for which  $dS = 0$  by definition). However, this increase tends to zero together with the level spacing; therefore in the quasicontinuous spectrum approximation entropy is conserved for the adiabatic process as well. In this approximation, it can be deduced that the probability distribution obeys a wave equation, the wave velocity being expressed in terms of the density of states. By constructing the solution of this equation in the standard way one sees that the adiabatic distribution is canonical (thus coinciding with the zero-polytropic one) if  $c_a$ , the heat capacity at constant external parameter, is  $a$  and  $T$  independent. Such system is “canonical” in the sense that it keeps the canonical distribution despite the absence of a thermostat. This holds in the classical limit for a system with quadratic degrees of freedom.

For a general case an adiabatic process differs from the relevant zero-polytropic one. However, it turns out that in the thermodynamic limit the mean values of energy for the two cases coincide (their relative difference is of the order of the inverse number of particles) while its fluctuations differ essentially (the relative difference of the fluctuation is the same as the change of  $c_a$  in the process). This difference in fluctuations should in principle be observable.

One point that has been left aside in this consideration is the estimate of the process speed necessary for our conclusions to take place. For the zero-polytropic process there is the usual condition that the process has to be quasistatic, which means there has to be enough time for equilibrium to be established at every moment. The same has to hold for the adiabatic process; enough time has to be provided for the equalization of probability to be accomplished at each level crossing. Besides, the conditions of applicability of the adiabatic theorem have to be fulfilled, which means that the process has to be slow enough for the state to “follow” the change of external parameters, in the quantum-mechanical sense. Provided that all these conditions are fulfilled, we come to the above-formulated conclusions: In general, the adiabatic process and the zero-polytropic process are *different*; for macroscopic systems this difference manifests itself in the fluctuations of energy, namely,

$$E_{\text{ad}}(a, T) = E_z(a, T), \quad (10.1)$$

$$\Delta E = \begin{cases} \sqrt{c_a(a, T)} T & \text{for the zero-polytropic process,} \\ \sqrt{c_a(a_0, T_0)} T & \text{for the adiabatic process.} \end{cases} \quad (10.2)$$

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