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ABSTRACT

A system of equations is given for the distribution of the fluctuations of arbitrary thermodynamic state variables, by exploiting the Riemannian structure of the thermodynamic state space. These equations have been made compatible with the Second Principle of Thermodynamics, and for small fluctuations they reproduce the usual Gaussian law. We show a real stochastic process resulting in these equations.

АННОТАЦИЯ

С помощью Римановой структуры пространства термодинамических состояний выводится система уравнений для распределения флуктуаций любой термодинамической величины. Полученные уравнения автоматически являются совместимыми со вторым началом термодинамики, и для маленьких флуктуаций они воспроизводят обычное гауссовское распределение. Показывается действительный стохастический процесс, приводящий к этим уравнениям.

KIVONAT

A termodinamikai állapottér Riemann-struktúráját felhasználva megadunk egy egyenletrendszert tetszőleges termodinamikai állapothatározó fluktuációinak eloszlására. Az egyenletek konstrukciójuknál fogva tiszteletben tartják a Második Főtételt, és kis fluktuációkra visszaadják a szokásos Gauss-eloszlást. Mutatunk olyan valódi stochasztikus folyamatot, mely ezen egyenletekre vezet.

1. INTRODUCTION

Statistical mechanics[1] yields a foundation of thermodynamics, which latter is obtained in the so-called thermodynamic limes, i.e. when the size of a given homogeneous equilibrium system goes to infinity. Then, of course, the fluctuations of the thermodynamic characteristics vanish.

When the system is macroscopic but finite, fluctuations appear in it with some probability distribution, and there exist thermodynamic expressions for their first and second momenta[2,3]. Thus, although the thermodynamic limit cannot yield all the informations about finite systems, one may expect thermodynamic formulation for the distribution of the fluctuations. In fact, various distributions can be constructed with differ in higher momenta; the first and simplest one was proposed by Einstein[2]. Here we want to formulate an equation for these distributions, which are slightly more complicated, but possess certain advantageous properties.

2. EVOLUTION EQUATION FOR THE EXTENSIVE FLUCTUATIONS

Consider a homogeneous equilibrium system of infinite volume. The thermodynamic state of this system is completely determined by the set of n independent extensive densities $\{x^i, i=1,2,\ldots,n\}$.

Take a subsystem of finite volume V. For it, the remainder of the infinite system is a reservoir. Denote the state of the reservoir by x_o^i and that of the finite subsystem by x^i. Obviously, x will fluctuate around x_o with certain probability $p_V(x|x_o)d^n x$.

When the subsystem is infinite too there are no fluctuations, i.e.

$$p_\infty(x|x_o) = \delta^{(n)}(x-x_o) \ . \tag{2.1}$$

We are looking for the function $p_V(x|x_o)$. First we derive a set of constraints for it from the Second Principle of Thermodynamics[4]. Obviously, the expectation values of x's must be independent of V, thus equal to the reservoir value:

$$\int x^i p_V(x|x_o) d^n x = x_o^i \ , \qquad i = 1,2,\ldots,n \ , \tag{2.2}$$

otherwise, after a fictitious separation of a great number of subsystems and rejoining them in a greater subsystem, this latter one would not be in macroscopic equilibrium with the reservoir. The Second Principle forbids this.

Now, there exists an approximative $p_V^G(x|x_o)$ for $p_V(x|x_o)$ if the fluctuations are small[2]:

$$p_V^G(x|x_o) = \left(\frac{V}{2\pi}\right)^{n/2} \sqrt{|g(x_o)|} \exp\left\{-\frac{V}{2} \sum_{i,k=1}^n g_{ik}(x_o)(x^i-x_o^i)(x^k-x_o^k)\right\} \ . \tag{2.3}$$

Here

$$g_{ik}(x) = -\frac{\partial^2 s(x)}{\partial x^i \partial x^k} \ , \qquad i,k=1,2,\ldots,n \ , \tag{2.4}$$

and $|g|$ denotes the determinant of g_{ik}.

There is no reason to believe the form (2.3) if x is far from x_o since g_{ik} is taken at x_o thus the distribution p_V^G is not affected by the global properties of the state space.

Nevertheless the leading terms seem correct, thus let us start with the Gaussian approximation of $p_V(x|x_o)$. Introducing a "time" variable $\tau, \tau=1/V$ instead of V, the Gaussian distribution $p^G(\tau,x|x_o) = p_V^G(x|x_o)$ fulfils a diffusion type evolution equation:

$$\frac{\partial}{\partial\tau} p^G(\tau,x|x_o) = g^{ik}(x_o) \frac{\partial^2}{\partial x^i \partial x^k} p^G(\tau,x|x_o) \tag{2.5}$$

where g^{ik} is the inverse matrix of g_{ik}, with the initial condition

$$p^G(0,x|x_0) = \delta^{(n)}(x-x_0) \ . \tag{2.6}$$

(Henceforth we adopt the Einstein convention: there is a summation if an index occurs twice, above and below.)

As we mentioned above the evolution equation should contain the local structure of the thermodynamic state space even for x's which are far from the initial x_0. In order to ensure this property we have to generalize the Gaussian equation (2.5).

We should use $g^{ik}(x)$ instead of $g^{ik}(x_0)$ in the eq. (2.5) and complete this expression with terms containing the derivatives of g^{ik}. We have to get total divergence on the rhs and to satisfy the constraints (2.2) as well. The only possible choice is then

$$\frac{\partial}{\partial\tau}p(\tau,x|x_0) = \frac{\partial^2}{\partial x^i\partial x^k}g^{ik}(x)p(\tau,x|x_0) \ . \tag{2.7}$$

This generalized evolution equation and the initial contition

$$p(0,x|x_0) = \delta^{(n)}(x-x_0) \tag{2.8}$$

are suggested to describe the probability distribution of the thermodynamic fluctuations in a given subsystem of finite volume $V=1/\tau$.

Consider finally the case when we are not interested in the distribution of the n'th extensive x^n, looking for the distribution $\tilde{p}(\tau,\tilde{x}|\tilde{x}_0)$ of $\tilde{x}\equiv(x^1,x^2,\ldots,x^{n-1})$:

$$\tilde{p}(\tau,\tilde{x}|\tilde{x}_0) = \int p(\tau,x|x_0)dx^n \ . \tag{2.9}$$

If one integrate the eqs. (2.7,8) by dx^n it can be shown that $\tilde{p}(\tau,\tilde{x}|\tilde{x}_0)$ obeys the same evolution equation as $p(\tau,x|x_0)$ does, with the substitutions: $n \to n-1$, $x \to \tilde{x}$.

3. EVOLUTION EQUATION FOR THE FLUCTUATION OF GENERAL VARIABLES

In the previous Section an equation was found for the fluctuations of extensive densities, which 1) is of quite natural form, 2) fulfils the Second Principle of Thermodynamics, and 3) yields the Gaussian approximation for large V.

Now, in many cases one is interested in the fluctuation of other quantities (as e.g. the intensives). Of course, these quantities are functions of the extensive densities, so the fluctuation probabilities can be determined through $p_V(x|x_o)$. Denote the extensive densities by x^i and a general complete set of other parameters by x^i, then

$$x^i = \varphi^i(x), \quad i=1,2,\ldots,n \ . \tag{3.1}$$

This is a coordinate transformation on the state space. Obviously the distribution of the new variables will be

$$p_V(x|x_o) = p_V(x|x_o) \left| \frac{\partial \varphi^i(x)}{\partial x^k} \right| \ . \tag{3.2}$$

Nevertheless, there is an other way too, namely to find an evolution equation directly for $p_V(x|x_o)$, and one has to see if the two p_V's are the same.

We adopt the idea that the thermodynamic state space is a Riemannian metric space. The metric tensor in extensive coordinates is defined by eq. (2.4)[5,6]. In order to get a unique distance in a coordinate transformation (3.1) g_{ik} must change according to the usual transformation law[7]

$$g_{ik}(x) = g_{rs}(x) \frac{\partial \varphi^r(x)}{\partial x^i} \frac{\partial \varphi^s(x)}{\partial x^k} \ . \tag{3.3}$$

Now, we need a covariant evolution equation for $p_V(x|x_o)$, because covariance automatically guarantees that the quantities change properly with the coordinate transformation, so then

$p_V(x|x_o)$ will be unique. Naturally, this covariant equation has to possess the form (2.7) in extensive coordinates. Since the Riemannian geometry[7] has a proper covariant formalism, henceforth we adopt its method.

Note first that $p_V(x|x_o)$ is not a scalar, since the covariant volume element is $\sqrt{|g|}d^n x$. Thus the scalar quantity is ρ,

$$\rho(\tau,x|x_o) = \frac{1}{\sqrt{|g(x)|}} \, p_V(x|x_o) \ . \tag{3.4}$$

Obviously the initial condition (2.8) is now

$$\rho(0,x|x_o) = \frac{1}{\sqrt{|g(x_o)|}} \, \delta^{(n)}(x-x_o) \ . \tag{3.5}$$

The form of eq. (2.7) shows that we need a diffusion type equation for ρ. We claim that the proper form is

$$\frac{\partial}{\partial\tau}\rho(\tau,x|x_o) = \Delta\rho(\tau,x|x_o) + \nabla_r(h^r(x)\rho(\tau,x|x_o)) \tag{3.6}$$

where ∇_i stands for the covariant derivative, Δ is the covariant Laplacian[7], and h^i is a vector field guaranteeing constraints (2.2):

$$\int \varphi^{i|}(x)\rho(\tau,x|x_o)\sqrt{|g(x)|}\,d^n x = \varphi^{i|}(x_o) \ . \tag{3.7}$$

Here the bar in $\varphi^{i|}$ denotes that i is not a vectorial index but a name.

By differentiating this equation with respect to τ, using eq. (3.6), and performing partial integrations, one gets

$$\int (\Delta\varphi^{i|} - \frac{\partial\varphi^{i|}}{\partial x^r} \, h^r)\rho\sqrt{|g|}\,d^n x = 0 \ . \tag{3.8}$$

Since this equation must hold for any ρ, the result is

$$\Delta\varphi^{i|} = \frac{\partial\varphi^{i|}}{\partial x^r} \, h^r \tag{3.9}$$

According to eq. (3.1), $\varphi^{i|}$ occurs in a coordinate transforma-
tion, so $\partial\varphi^{i|}/\partial x^k$ must possess a regular matrix and the vector
field h^i is then uniquely determined by eq. (3.9).

Eqs. (3.6), (3.9) are covariant. In extensive coordinates
eq. (3.9) takes the form

$$h^i = \frac{1}{\sqrt{|g|}} \partial_r (g^{rs}\sqrt{|g|}\partial_s\varphi^i) \tag{3.10}$$

while eq. (3.6) can be written as

$$\frac{\partial}{\partial\tau} p = \partial_r \left\{ g^{rs}\sqrt{|g|}\partial_s (\frac{p}{\sqrt{|g|}}) + h^r \frac{p}{\sqrt{|g|}} \right\} , \tag{3.11}$$

$$p = \sqrt{|g|}\rho .$$

By combining eqs. (3.10) and (3.11) they reduce to eq. (2.7).
Thus eqs. (3.4-6), (3.9) are the covariant forms of the evolu-
tion equation (2.6-7).

4. STOCHASTIC FOUNDATION OF THE EVOLUTION EQUATION

In the previous two sections we proposed a new evolution
equation which would govern the distribution of the thermo-
dynamic fluctuations arising in finite equilibrium systems. An
elegant form of covariant diffusion equation on the Riemann
metricized state space was found.

Here we are going to show that this diffusion comes from a
true stochastic process which is accomplished on the state space.

Originally, when Ruppeiner[5] supplied thermodynamic state
space with Riemannian metric (2.4) he also outlined a stochastic
process. But he did not vary the volume of his system thus the
physical realization of his construction was not quite clear.

Consider a homogeneous closed equilibrium system $\Omega(V,x)$ of
volume V and extensive densities $x\equiv(x^1,x^2,\ldots,x^n)$. Now, at
random, let us choose and separate a subsystem $\Omega(V',x')$ in it:

$$\Omega(V',x')\subseteq\Omega(V,x) , \qquad V'\leq V , \tag{4.1}$$

and denote the probability of finding x' at a given value by $P(V',x'|V,x)d^n x'$.

Obviously,

$$P(V,x'|V,x) = \delta^{(n)}(x'-x) \ . \tag{4.2}$$

Repeating the above procedure and choose a subsystem $\Omega(V'',x'')$ in $\Omega(V',x')$, we get the conditional distribution $P(V'',x''|V',x')$ for x''. It can obviously be supposed that the final distribution of x'', i.e.

$$\int P(V'',x''|V',x')P(V',x'|V,x)d^n x' \tag{4.3}$$

is not affected by the intermediate separation of $\Omega(V',x')$. Therefore the probability (4.3) must be equal to the probability distribution of x'' in a subsystem $\Omega(V'',x'')$ which was directly choosen from $\Omega(V,x)$:

$$\int P(V'',x''|V',x')P(V',x'|V,x)d^n x' = P(V'',x''|V,x) \ ,$$
$$V'' \leq V' \leq V \ . \tag{4.4}$$

Equations (4.2), (4.4) show that the process of continuously diminishing the volume of a homogeneous equilibrium system can be considered as a continuous Markovian stochastic process[8]. The role of stochastic variable is played by the state coordinate x of the actual system. The volume reduction must be adiabatic, i.e. slower than the relaxation of the thermodynamic fluctuations.

Now let us suppose that this stochastic process is of finite variance and thus it is governed by the Fokker-Planck-Kolmogorov differential equation[8].

In order to find the coefficients of the differential equation we have to calculate the following two limits:

$$\lim_{V' \to V} \frac{\langle x'^i - x^i \rangle}{V - V'} \equiv \lim_{V' \to V} \int \frac{x'^i - x'}{V - V'} P(V',x'|V,x)d^n x' \ , \tag{4.5}$$

$$\lim_{V' \to V} \frac{<(x'^i - x^i)(x'^k - x^k)>}{V - V'} \equiv \lim_{V' \to V} \int \frac{(x'^i - x^i)(x'^k - x^k)}{V - V'} P(V', x' | V, x) d^n x' .$$

(4.6)

The expression (4.5) is obviously zero since the Second Principle requires that

$$<x'^i> = x^i .$$

(4.7)

As for the expression (4.6), we should know the correlation of the extensive densities x'^i of the subsystem $\Omega(V', x') \subset \Omega(V, x)$. The problem is that in (4.6) $V' \to V$ and thus $\Omega(V', x')$ cannot be a small subsystem of $\Omega(V, x)$. But we can easily avoid this trap using the complementary system $\Omega(\bar{V}, \bar{x}) = \Omega(V, x) \setminus \Omega(V', x')$ which is already a small subsystem. It is known that the correlation of the extensive densities $\bar{x}^i$ in such a small subsystem is given as follows[2,3]:

$$<(\bar{x}^i - x^i)(\bar{x}^k - x^k)> = -\frac{1}{\bar{V}} g^{ik}(x)$$

(4.8)

where $g^{ik}(x)$ is the inverse of the matrix $g_{ik}(x)$, see definition (2.4).

Now using the balance equation

$$\bar{V}\bar{x} + (V - \bar{V})x' = Vx$$

(4.9)

we can eliminate x' from the expression (4.6) and we get instead:

$$\lim_{\bar{V} \to 0} \frac{1}{\bar{V}} \left\langle \left(\frac{\bar{V}}{V - \bar{V}}\right)^2 (\bar{x}^i - x^i)(\bar{x}^k - x^k) \right\rangle = -\frac{1}{V^2} g^{ik}(x) .$$

(4.10)

This expression is the coefficient function in the Fokker-Planck-Kolmogorov equation:

$$\frac{\partial}{\partial V'} P(V', x' | V, x) = \frac{\partial^2}{\partial x'^i \partial x'^k} \left(-\frac{1}{V^2} g^{ik}(x') P(V', x' | V, x)\right) .$$

(4.11)

In the variable τ ($\tau=1/V$) the same equation is of the following form:

$$\frac{\partial}{\partial\tau'} P(\tau',x'|\tau,x) = \frac{\partial^2}{\partial x'^i \partial x'^k} (g^{ik}(x')P(\tau',x'|\tau,x)) \qquad (4.12)$$

and the initial condition (4.2) will be as
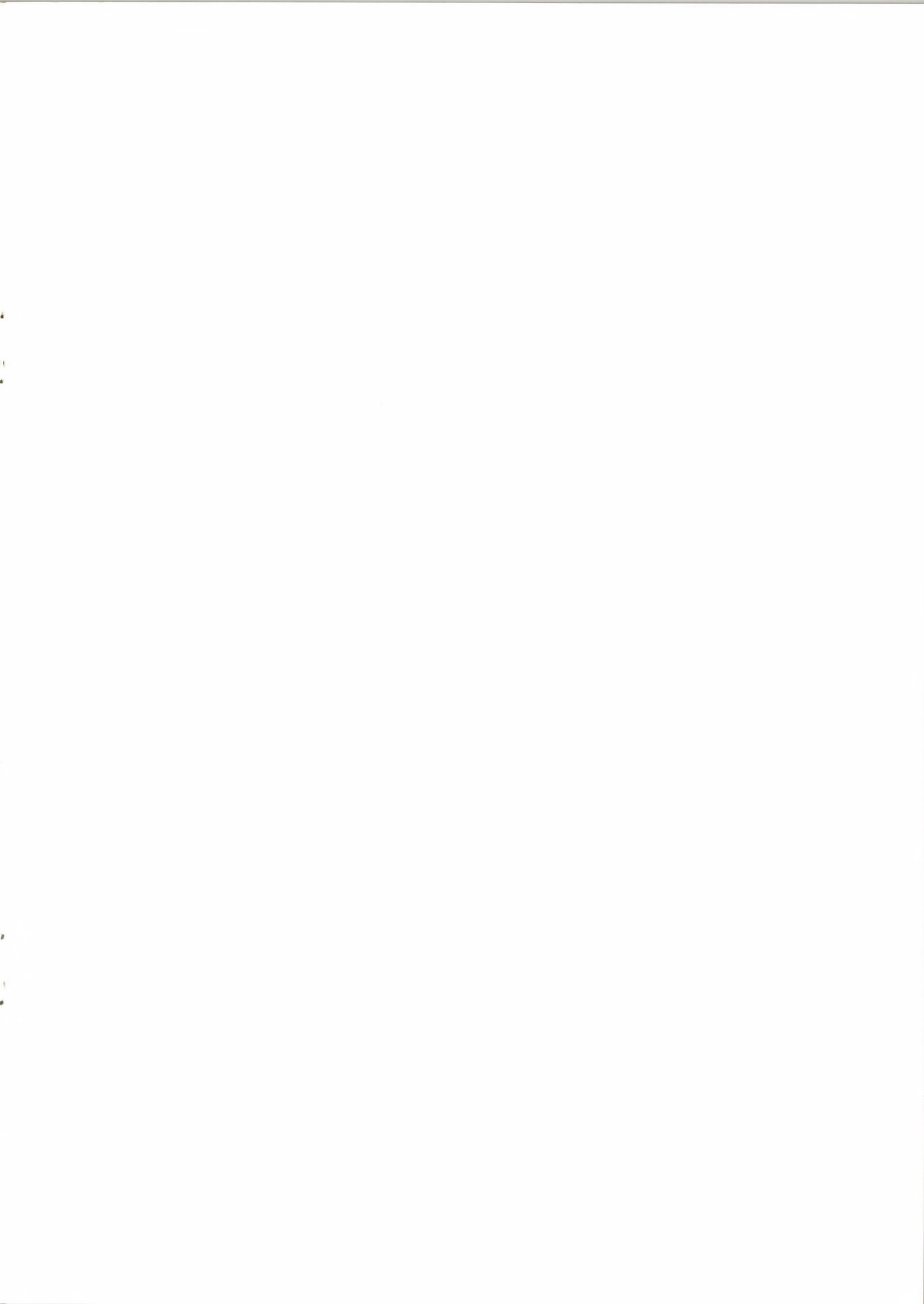
$$P(\tau,x'|\tau,x) = \delta^{(n)}(x'-x) . \qquad (4.13)$$

It is just the proper moment to note that the distribution $p_V(x|x_o)$ defined in Section 2 corresponds obviously to the transition probability $P(V,x|\infty,x_o)$ and thus $p(\tau,x|x_o)$ of Section 2 is equal to $P(\tau,x|0,x_o)$ in variable τ. Therefore equations (4.12), (4.13) yield the evolution equations (2.7), (2.8) which were introduced in a formal way in Section 2, and also the covariant form (3.6), (3.9) of the evolution equation gets its stochastic foundations.

5. CONCLUSION

We have proposed a covariant system of equations for the fluctuations of thermodynamic characteristics. For small fluctuations they reproduce the usual Gaussian distribution, and from practical viewpoint the difference is small compared to any other possible distribution too. Nevertheless, because of the covariance our equations can be directly used in arbitrary variables. In addition, the Second Principle of Thermodynamics automatically holds too. The equations presented here are the simplest possible ones possessing these theoretically important properties.

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