Covariant evolution equation for the thermodynamic fluctuations

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Recently, by exploiting the Riemannian structure of the thermodynamic state space, a system of equations was given for the distribution of the fluctuations of arbitrary thermodynamic state variables. Here we present an alternative version of the theory, which incorporates explicitly the balance equations for the extensive parameters. For small fluctuations the usual Gaussian law is reproduced.

I. INTRODUCTION

Statistical mechanics[1] yields a foundation for thermodynamics, through the so-called thermodynamic limit. Here, of course, the fluctuations of the thermodynamic characteristics vanish.

When the system is macroscopic but finite, fluctuations appear with some probability distribution, and thermodynamic expressions can be derived for their first and second moments.[2,3] Thus, although the thermodynamic limit cannot give all the information on finite systems, one may expect a thermodynamic formulation for the distribution of fluctuations. In fact, various distributions can be constructed which differ in higher moments; the first and simplest one was proposed by Einstein.[2]

However, the Einstein theory cannot yield a realistic distribution for large fluctuations, and it also fails for systems of the size of about the correlation volume. We must add that, originally, Einstein himself regarded his formula as a mere approximation to the true distribution.[2]

It is also unclear if the distribution of the fluctuations should be calculated as a function of the extensive parameters or can be expressed in terms of arbitrary thermodynamic variables.

Recently, Ruppeiner[4] introduced a Riemannian structure in the thermodynamic state space, which enables us to formulate coordinate-invariant relations. Obviously, the probability of the fluctuations must be independent of the actual coordinate system; if the Riemannian structure has indeed a deep physical meaning,[5] the probability must be expressed by a covariant formula.

In fact, Ruppeiner[6] presented a covariant expression whose $V\to\infty$ limit is equivalent to the Gaussian approximation of Einstein's theory. His distribution function satisfies the same differential equation as the Gaussian approximation, but partial derivatives were replaced by covariant ones. In another paper[7] a path-integral formalism gave the same distribution function. Here, the "comma-goes-to-semicolon rule" was not used; instead, a covariant "fluctuation hypothesis" was adopted from a recent theory[8] of nonlinear relaxation processes.

Here we are going to construct an alternative fluctuation formula, which is also cast into covariant form. It is somewhat more complicated, but as a reward, it automatically conserves balance for the extensive thermodynamic characteristics.

In Sec. II we formulate, in extensive coordinates, the equations which must be satisfied by the fluctuation probability; Sec. III gives the covariant formulation of the same equations. In Sec. IV we repeat Ruppeiner's stochastic construction without assuming either the comma-goes-to-semicolon rule or the fluctuation hypothesis.

II. 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 this, the remainder of the infinite system is a reservoir. Denote the state of the reservoir with x_0^i and that of the finite subsystem with x^i. Obviously, x will fluctuate around x_0 with certain probability $p_V(x\mid x_0)d^nx$.

The most delicate assumption in the new thermodynamic fluctuation theory is that p depends only on the thermodynamic quantities x^i, x_0^i, and V; thus all geometric and wall effects should be negligible. In this section, for the sake of simplicity, the reservoir system is taken to be infinite; the more general case will be discussed in Sec. IV. When the subsystem is also infinite there will be no fluctuations, i.e.,

$$p_\infty(x\mid x_0)=\delta^{(n)}(x-x_0)\ . \tag{2.1}$$

Now, we turn to the function $p_V(x\mid x_0)$. Observe that the actual variables are extensive densities. By definition, extensive parameters are additive, so their expectation values in a homogeneous system must be proportional to the volume; in our case the coefficients of proportionality are obviously the x_0^i's. Therefore, a fluctuation law is consistent with the balance equations only if

$$\int x^i p_V(x\mid x_0)d^nx\equiv x_0^i,\quad i=1,2,\ldots,n\ . \tag{2.2}$$

Now, there exists an approximate $p_V^G(x\mid x_0)$ for $p_V(x\mid x_0)$ if fluctuations are small:[2]

$$p_V^G(x\mid x_0)=\left[\frac{V}{2\pi}\right]^{n/2}\sqrt{|g(x_0)|}\times\exp\left[-\frac{V}{2}\sum_{i,k=1}^{n}g_{ik}(x_0)(x^i-x_0^i)\times(x^k-x_0^k)\right], \tag{2.3}$$

where coefficients g_{ik} are derived from the entropy density s,

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

and $|g|$ denotes the determinant of g_{ik}. This probability function fulfills the constraints (2.2).

There is no reason to retain the form (2.3) if x is far from x_0 since g_{ik} is taken at x_0; thus, the distribution p_V^G is not affected by the global properties of the state space.

Nevertheless, the leading terms seem correct; thus, we may start with the Gaussian approximation of $p_V(x\mid x_0)$. Introducing a "time" variable $\tau=1/V$ instead of V, the Gaussian distribution $p^G(\tau,x\mid x_0)=p_V^G(x\mid x_0)$ fulfills a diffusion-type evolution equation:[6]

$$\frac{\partial}{\partial\tau}p^G(\tau,x\mid x_0)=g^{ik}(x_0)\frac{\partial^2}{\partial x^i\partial x^k}p^G(\tau,x\mid x_0), \tag{2.5}$$

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

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

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

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

Obviously, in Eq. (2.5) we should use $g^{ik}(x)$ instead of $g^{ik}(x_0)$ and complete this expression with terms containing the derivatives of g^{ik}. We have to obtain total divergence on the right-hand side and satisfy the constraints (2.2) at the same time. The only possible choice is then

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

We suggest this generalized evolution equation and the initial condition

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

as describing the probability distribution of the fluctuation of the extensive thermodynamic parameters in a given subsystem of finite volume $V=1/\tau$. Obviously, as $V\to\infty$ ($\tau\to 0$) and g_{ik} is more and more constant in the expected range of fluctuations, Eq. (2.7) becomes equivalent with the usual Gaussian law (2.5).

Finally, consider the case when we are not interested in the distribution of the nth extensive x^n, looking for the distribution $\tilde{p}(\tau,\tilde{x}\mid\tilde{x}_0)$ of $\tilde{x}\equiv(x^1,x^2,\ldots,x^{n-1})$:

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

By integrating Eqs. (2.7) and (2.8) by dx^n, if $g^{ik}{}_{,n}\equiv 0$, it can be shown that $\tilde{p}(\tau,\tilde{x}\mid\tilde{x}_0)$ obeys the same evolution equation as $p(\tau,x\mid x_0)$ does, with the substitutions $n\to n-1$, $x\to\tilde{x}$. This attractive feature is absent in the previous version of the new thermodynamic fluctuation theory.[6,7]

III. EVOLUTION EQUATION FOR THE FLUCTUATION OF GENERAL VARIABLES

In Sec. II an equation was proposed for the fluctuations of extensive densities, which (1) is of quite natural form, (2) conserves the extensive parameters in mean, and (3) yields the Gaussian approximation for large volumes. Now, we adopt the idea[4] that the thermodynamic state space is a Riemannian metric space and require that the fluctuation formula be covariant.

Let us introduce a general complete set of parameters $\mathcal{x}^i$ instead of the extensive densities

$$x^i=\varphi^i(\mathcal{x}) \tag{3.1}$$

and the metric

$$g_{ik}(\mathcal{x})=g_{rs}(x)\frac{\partial\varphi^r}{\partial\mathcal{x}^i}\frac{\partial\varphi^s}{\partial\mathcal{x}^k}. \tag{3.2}$$

The distribution function p of the general parameter $\mathcal{x}$ can be written in the following form:

$$p_V(\mathcal{x}\mid\mathcal{x}_0)=\rho(\tau,\mathcal{x}\mid\mathcal{x}_0)\sqrt{|g(\mathcal{x})|}, \tag{3.3}$$

where ρ is a Riemannian scalar field while p is not. Obviously, the initial condition for ρ is

$$\rho(0,\mathcal{x}\mid\mathcal{x}_0)=\frac{1}{\sqrt{|g(\mathcal{x}_0)|}}\delta^{(n)}(\mathcal{x}-\mathcal{x}_0). \tag{3.4}$$

The form of Eq. (2.7) would suggest a covariant Laplacian equation. However, if Eq. (2.7) holds in extensive coordinates, then the covariant equation for ρ definitely cannot be a pure Laplacian. Furthermore, a Laplacian equation would not be consistent with the constraints (2.2). Therefore we claim that the proper covariant form must also contain a drift term:[9]

$$\frac{\partial}{\partial\tau}\rho(\tau,\mathcal{x}\mid\mathcal{x}_0)=\Delta\rho(\tau,\mathcal{x}\mid\mathcal{x}_0)+\nabla_i(h^i(\mathcal{x})\rho(\tau,\mathcal{x}\mid\mathcal{x}_0)), \tag{3.5}$$

where ∇_i stands for the covariant derivative, Δ is the covariant Laplacian,[10] and h^i is a vector field guaranteeing constraints (2.2),

$$\int\varphi^{i\,|}(\mathcal{x})\rho(\tau,\mathcal{x}\mid\mathcal{x}_0)\sqrt{|g(\mathcal{x})|}\,d^n\mathcal{x}\equiv\varphi^i(\mathcal{x}_0). \tag{3.6}$$

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. (3.5), and performing partial integrations, one arrives at

$$\int\left[\Delta\varphi^{i\,|}-\frac{\partial\varphi^{i\,|}}{\partial\mathcal{x}^r}h^r\right]\rho\sqrt{|g|}\,d^n\mathcal{x}=0. \tag{3.7}$$

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

$$\Delta\varphi^{i\,|}=\frac{\partial\varphi^{i\,|}}{\partial x^r}h^r\ . \tag{3.8}$$

According to Eq. (3.1), $\varphi^{i\,|}$ occurs in a coordinate transformation, so $\partial\varphi^{i\,|}/\partial x^k$ must possess a regular matrix, and the vector field h^i is then uniquely determined by Eq. (3.8).

Equations (3.5) and (3.8) are covariant. In extensive coordinates Eq. (3.8) gives

$$h^i=\frac{1}{\sqrt{|g|}}\partial_r(g^{ri}\sqrt{|g|}) \tag{3.9}$$

and Eq. (3.5) can be written as

$$\frac{\partial}{\partial\tau}p=\partial_r\left[g^{rs}\sqrt{|g|}\,\partial_s\frac{p}{\sqrt{|g|}}+h^r\frac{p}{\sqrt{|g|}}\right]\ . \tag{3.10}$$

By combining Eqs. (3.9) and (3.10) they reduce to Eq. (2.7). Thus Eqs. (3.3)—(3.5) and (3.8) are the covariant forms of the evolution equations (2.7) and (2.8).

IV. STOCHASTIC FOUNDATION OF THE EVOLUTION EQUATION

In Secs. II and III we proposed a new evolution equation governing the distribution of the thermodynamic fluctuations arising in finite equilibrium systems. An elegant form of the covariant diffusion equation on the Riemannian metricized state space was found. It can be shown[7] that this diffusion comes from a true stochastic process which is accomplished on the state space.

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:

$$\Omega(V',x')\subseteq\Omega(V,x),\quad V'\le V \tag{4.1}$$

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

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

Repeating the above procedure and choosing a subsystem $\Omega(V'',x'')$ in $\Omega(V',x')$, we obtain the conditional distribution $P(V'',x''\,|\,V',x')$ for x''. It can obviously be supposed[6,7] that the final distribution of x'', i.e.,

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

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 is directly chosen from $\Omega(V,x)$:

$$\int P(V'',x''\,|\,V',x')P(V',x'\,|\,V,x)d^nx'=P(V'',x''\,|\,V,x)\ ,\qquad V''\le V'\le V\ . \tag{4.4}$$

Equations (4.2) and (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.[11] The role of stochastic variable is played by the state coordinate x of the actual system.

Now, suppose that this stochastic process is of finite variance. Then it should be governed by the Fokker-Planck-Kolmogorov differential equation:

$$\frac{\partial}{\partial V'}(V',x'\,|\,V,x)=\left[-\frac{\partial^2}{\partial x'^i\partial x'^k}G^{ik}(V',x')+\frac{\partial}{\partial x'^i}H^i(V',x')\right]P(V',x'\,|\,V,x)\ . \tag{4.5}$$

The solution to this equation can be formally expressed by path integrals.[12,13]

In order to find the coefficients of the differential equation, we have to consider the following two limits:[11]

$$G^{ik}(V,x)\equiv\lim_{V'\to V}\frac{\langle(x'^i-x^i)(x'^k-x^k)\rangle}{V-V'}=\lim_{V'\to V}\int\frac{(x'^i-x^i)(x'^k-x^k)}{V-V'}\times P(V',x'\,|\,V,x)d^nx'\ , \tag{4.6}$$

$$H^i(V,x)\equiv\lim_{V'\to V}\frac{\langle x'^i-x^i\rangle}{V-V'}=\lim_{V'\to V}\int\frac{x'^i-x^i}{V-V'}P(V',x'\,|\,V,x)d^nx'\ . \tag{4.7}$$

As a consequence of the balance equations, the expression (4.7) is zero [see constraints (2.2)].

As for the expression (4.6), one should know the correlation of the extensive densities x'^i of the subsystem $\Omega(V',x')\subseteq\Omega(V,x)$. Here, we encounter the problem that in (4.6) $V'\to V$ and thus $\Omega(V',x')$ cannot be a small subsystem of $\Omega(V,x)$. Nevertheless, we can easily circumvent this difficulty by using the complementary system $\Omega(\bar V,\bar x)\equiv\Omega(V,x)\setminus\Omega(V'x')$ which is already a small subsystem. It is well-known that the correlation of the extensive densities $\bar x^i$ in such a small subsystem is given as[2,3]

$$\langle(\bar x^i-x^i)(\bar x^k-x^k)\rangle=\frac{1}{\bar V}g^{ik}(x)\ , \tag{4.8}$$

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

Now using the balance equation

$$\bar V\bar x+(V-\bar V)x'=Vx \tag{4.9}$$

we can eliminate x' from the expression (4.6), and we obtain instead

$$G^{ik}(V,x)=\lim_{\bar V\to 0}\frac{1}{\bar V}\left\langle\left[\frac{V}{V-\bar V}\right]^2(\bar x^i-x^i)(\bar x^k-x^k)\right\rangle=\frac{1}{V^2}g^{ik}(x)\ . \tag{4.10}$$

This is the only nonzero coefficient function in the Fokker-Planck-Kolmogorov equation (4.5):

$$\frac{\partial}{\partial V'}P(V',x' \mid V,x)$$
$$= -\frac{\partial^2}{\partial x''^i \partial x''^k}\frac{1}{V'^2}g^{ik}(x')P(V',x' \mid V,x) . \quad (4.11)$$

In the variable $\tau = 1/V$ the same equation takes the following form:

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

and the appropriate initial condition (4.2) is

$$P(\tau,x' \mid \tau,x) = \delta^{(n)}(x'-x) . \quad (4.13)$$

At this point, we note that the distribution $p_V(x \mid x_0)$ defined in Sec. II obviously corresponds to the transition probability $P(V,x \mid \infty,x_0)$ and, as a result, $p(\tau,x \mid x_0)$ of Sec. II is equal to $P(\tau,x \mid 0,x_0)$ in variable τ. Therefore Eqs. (4.12) and (4.13) yield the evolution equations (2.7) and (2.8) which were introduced in a formal way in Sec. II, and also the covariant form (3.3)—(3.5) and (3.8) of the evolution equation gains its stochastic foundation. Note that without the constraints (2.2) the drift coefficients H^i of the Fokker-Planck-Kolmogorov equation would remain undefined.

V. CONCLUSION

We have derived a covariant system of equations for the fluctuations of thermodynamic characteristics. For small fluctuations they reproduce the usual Gaussian distribution. In addition, the balance equations for the extensive parameters hold automatically. Because of the covariance, our equations can be directly used in arbitrary variables. Our fluctuation formulas represent a modified version of Ruppeiner's equations. It is interesting to note that, although the formulation is covariant, the equations have their simplest form in extensive coordinates.

[1]L. D. Landau and E. M. Lifshits, *Statistical Physics* (Pergamon, London, 1958).
[2]A. Einstein, Ann. Phys. (Leipzig) **33**, 1275 (1910).
[3]R. F. Greene and H. B. Callen, Phys. Rev. **83**, 1231 (1951).
[4]G. Ruppeiner, Phys. Rev. A **20**, 1608 (1979).
[5]L. Diósi *et al.*, Phys. Rev. A **29**, 3343 (1984).
[6]R. Ruppeiner, Phys. Rev. Lett. **50**, 287 (1983).
[7]G. Ruppeiner, Phys. Rev. A **27**, 1116 (1983).
[8]H. Grabert and M. S. Green, Phys. Rev. A **19**, 1747 (1979).
[9]The drift term is the simplest divergence without higher derivatives. See Ref. 13.
[10]L. P. Eisenhart, *Riemannian Geometry* (Princeton University, Princeton, N.J., 1926).
[11]B. V. Gnedenko, *The Theory of Probability* (Mir, Moscow, 1969).
[12]R. Graham, Z. Phys. B **26**, 281 (1977).
[13]H. Dekker, Phys. Rev. A **24**, 3182 (1981).