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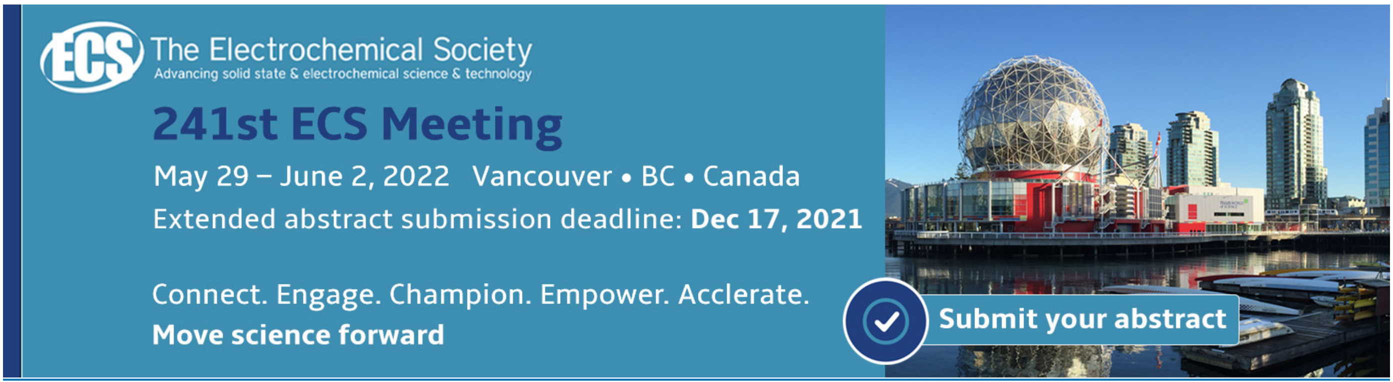

Advanced selection of ensemble control tools

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Abstract. We propose a method for generating a wide variety of increasingly complex microscopic temperature expressions in the form of functional polynomials in thermodynamic temperature. The motivation for study of such polynomials comes from thermostat theory. The connection of these polynomials with classical special functions, in particular, with Appell sequences, is revealed.

1. Introduction

Molecular dynamics (MD) [1–4] is an inevitable companion of research in a range of disciplines in natural sciences including the design of new functional materials and the drug discovery. MD simulations are performed under certain conditions, usually at fixed temperature and pressure. The concept of thermodynamic temperature is phenomenological in nature, but MD experiments should measure temperature as an average over time. Thus, we need a function of dynamic variables such that the temperature can be expressed by averaging this function over time along the trajectory in phase space of the system under a certain assumption of ergodicity. However, there is no any unique dynamic variables function corresponding to the thermodynamic temperature, but its alternate forms are possible. In this regard, it is not surprising that various dynamic temperature control schemes have been proposed and implemented in equations of motion in the form of mathematical tools, called the thermostat, which can be both deterministic and stochastic [4–9]. In applications, thermostat schemes as proposed in articles [10–12] are widely used, along with a number of built according to the methodology proposed in article [13]. These deterministic thermostats allow the generation of canonical density related to the simulated physical system using one additional degree of freedom, but their reliability is based on the ergodic hypothesis [14, 15]. This hypothesis equates the long-time average of a physical observable to the ensemble mean. While it is known that deterministic thermostats often violate ergodicity, they are assumed to be applicable for practical purposes. To improve the ergodicity of deterministic thermostats, a number of their modifications have been proposed [13, 16–20]. On the other hand, many studies have been done on the ergodicity violation of deterministic thermostats applied to low-dimensional systems, primarily to the harmonic oscillator [21–25], where rigorous results have been obtained [26, 27].

Our approach [28–30] to designing thermostatted dynamics of a physical system differs structurally in such a way that mathematical tools for dynamic control of a statistical ensemble are derived based on physical assumptions, rather than formal mathematical manipulations. This approach is ultimately grounded on the concept of temperature expression.

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In this article, we propose a method for obtaining a wide variety of increasingly complex temperature expressions. We say temperature expressions, but the ability to sample a canonical ensemble at a specific temperature also implies the ability to sample arbitrary probability measures. Thus, our analysis is broader than just a thermostat.

2. The dynamic ensemble control concept at a glance

The development of dynamic ensemble control tools is based on certain assumptions about the interaction between physical systems and the surrounding heat reservoir maintaining a constant temperature, leading to the concept of temperature expression [28]. Let us briefly review the details of corresponding theoretical scheme, which are essential for this article.

It is assumed that the physical system, S, placed in the thermal reservoir, Σ, (such that is considered as a dynamical system of a very large (infinite) number of phase variables, which determines the general statistical properties of the S system) should to some extent perturb it and will itself be affected by the backward influence of this perturbation. The energy of S and S^* systems interacting with the unperturbed part of the heat reservoir $\Sigma \setminus \mathrm{S}^*$ can fluctuate, while the temperature of reservoir $\Sigma \setminus \mathrm{S}^*$ remains constant, determining the general statistical properties of the entire system. Thus, the thermal reservoir is naturally divided into two parts, namely, the part that involved in joint dynamics with S system, S^*, and the unperturbed part, $\Sigma \setminus \mathrm{S}^*$, which is constantly in thermal equilibrium. An important assumption is made that all systems participating in joint dynamics are statistically independent at thermal equilibrium. In such a scheme, an additional thermostat variables are associated with the perturbed part S^* of the thermal reservoir. Therefore, the dynamic temperature control associated with the system S^* and its degrees of freedom is just as important to the theory as the temperature control of the system S. Of course, the actual description of S^* system depends on the physical system of interest to us, as well as on the experimental methods used to extract the information, as they determine the temporal and spatial scales of data measurement and interpretation.

Let the probability density $\sigma(x)$, $x \in \mathcal{M} = \mathbb{R}^n$ be given, where the phase space of the system S, $\mathcal{M}$, is not necessarily even-dimensional. Define the function $\mathcal{V}(x) : \mathcal{M} \to \mathbb{R}$,

$$\mathcal{V}(x) \propto -\vartheta \ln \sigma(x),$$

where $\vartheta > 0$ is a parameter, so that $\mathcal{V}(x)$ is a sufficiently smooth function, bounded from below and growing at infinity, $\mathcal{V}(x) \geq a\,|x|^b$ for some $a > 0$, $b > 0$, that is, a coercive function. We now define the probability density,

$$\sigma_\vartheta(x) \propto \exp\left\{-\vartheta^{-1}\mathcal{V}(x)\right\}, \quad x \in \mathcal{M} = \mathbb{R}^n, \tag{1}$$

instead of $\sigma(x)$. Thus, we consider a wider range of densities than is usual in the thermostat literature, since we mean further application of the method to gradient systems as well as applications beyond the physics. However, these issues should be treated separately.

Consider a pair of vector fields, the potential $\boldsymbol{\nabla}\mathcal{V}(x)$ and incompressible $\boldsymbol{G}(x)$, that is, $\boldsymbol{\nabla} \cdot \boldsymbol{G}(x) = 0$ for all $x \in \mathcal{M}$, such that

$$\boldsymbol{\nabla}\mathcal{V}(x) \cdot \boldsymbol{G}(x) = 0 \quad \text{for all} \quad x \in \mathcal{M}, \tag{2}$$

in other words, $\boldsymbol{\nabla}\mathcal{V}(x)$ and $\boldsymbol{G}(x)$ form a cosymmetric pair as described in [31]. The concept of cosymmetry has a deep mathematical content [32]. Then we associate the system S with the equations of motion,

$$\dot{x} = \boldsymbol{G}(x). \tag{3}$$

Thus, we arrive at the following properties, $\dot{\mathcal{V}} = \boldsymbol{\nabla}\mathcal{V}(x) \cdot \boldsymbol{G}(x) = 0$ and $\boldsymbol{\nabla} \cdot (\boldsymbol{G}(x)\,\sigma(x)) = 0$, that is, $\mathcal{V}(x)$ is a first integral and the density $\sigma(x)$ is invariant for the dynamics (3).

Examples of cosymmetric pairs $(\boldsymbol{G}(x), \boldsymbol{\nabla}\mathcal{V}(x))$ include:

1) $\boldsymbol{G}(x) = \mathbf{0}$ (trivial case), it may be useful in context of the gradient dynamical systems (will be discussed elsewhere);

2) $\boldsymbol{G}(\boldsymbol{x}) = \boldsymbol{\Lambda}\boldsymbol{\nabla}\mathcal{V}(x)$, where $\boldsymbol{\Lambda}$ is an antisymmetric matrix; a particular case is $\boldsymbol{\Lambda} = \mathbf{J}$ (symplectic unit), that is, the Hamiltonian system in even-dimensional phase space;

3) $\boldsymbol{G}(\boldsymbol{x}) = \boldsymbol{\Lambda}(x)\boldsymbol{\nabla}\mathcal{V}(x))$, where $\boldsymbol{\Lambda}(x)$ is a linear antisymmetric operator (matrix) depending on x; a particular case is an antisymmetric operator $\boldsymbol{\Lambda}(x)$ satisfying the Jacobi identity, that is, the Poisson system.

In all these cases, the vector fields are incompressible.

The case of Hamiltonian systems, that is, $\boldsymbol{G}(\boldsymbol{x}) = \mathbf{J}\boldsymbol{\nabla}H(x)$, where $H(x)$ is Hamiltonian and $x \in \mathcal{M} = \mathbb{R}^{2n}$, is mainly considered in the literature. However, thermostatically controlled gradient systems are also of interest for applications [30], in particular for problems beyond physics.

A similar description can be made with respect to the system S^*, considered as an isolated system.

Suppose the system S^* is not empty, that is, $n^* \geq 1$. Let us associate this system with the probability density,

$$\sigma^*_\vartheta(y) \propto \exp\left\{-\vartheta^{-1}\mathcal{V}^*(y)\right\}, \quad y \in \mathcal{M}^* = \mathbb{R}^{n^*}, \tag{4}$$

where $\mathcal{M}^*$ is the phase space of the system $\mathrm{S}^*$and it is supposed that $\mathcal{V}^*(y)$ is a sufficiently smooth function, bounded from below and growing at infinity, $\mathcal{V}^*(y) \geq a^* |x|^{b^*}$ for some $a^* > 0$, $b^* > 0$ (coercive function).

Let us consider a pair of vector fields, the potential $\boldsymbol{\nabla}_y\mathcal{V}^*(y)$ and incompressible $\boldsymbol{G}^*(y)$, that is, $\boldsymbol{\nabla}_y \cdot \boldsymbol{G}^*(y) = 0$ for all $y \in \mathcal{M}^*$, such that $\boldsymbol{\nabla}_y\mathcal{V}^*(y)$ and $\boldsymbol{G}^*(y)$ form a cosymmetric pair [31],

$$\boldsymbol{\nabla}_y\mathcal{V}^*(y) \cdot \boldsymbol{G}^*(y) = 0 \quad \text{for all} \quad y \in \mathcal{M}^*, \tag{5}$$

and associate the system S^* with the equations of motion,

$$\dot{y} = \boldsymbol{G}^*(y). \tag{6}$$

Thus, we find that $\dot{\mathcal{V}}^* = \boldsymbol{\nabla}_y\mathcal{V}^*(y) \cdot \boldsymbol{G}^*(y) = 0$ and $\boldsymbol{\nabla}_y \cdot (\boldsymbol{G}^*(y)\,\sigma^*_\vartheta(y)) = 0$, that is, $\mathcal{V}^*(y)$ is a first integral and the density $\sigma^*_\vartheta(y)$ is invariant for the dynamics (6).

Further, in order to consider the interaction and joint motion of systems S and S^* as described above, we first need to define the dynamical system, $\mathrm{S}^+ = \left(\mathcal{M}^+, \boldsymbol{G}^+(x, y)\right)$, which is a direct product of non-interacting (isolated) dynamical systems $\mathrm{S} = (\mathcal{M}, \boldsymbol{G}(x))$ and $\mathrm{S}^* = (\mathcal{M}^*, \boldsymbol{G}^*(y))$, that is, $\mathrm{S}^+ = \mathrm{S} \times \mathrm{S}^* = (\mathcal{M} \oplus \mathcal{M}^*, \boldsymbol{G}(x) \times \boldsymbol{G}^*(y))$. In other words, we consider a simple combination of two independent systems into one so that $z = (x, y) \in \mathcal{M}^+ = \mathcal{M} \oplus \mathcal{M}^*$ and

$$\dot{z} = \boldsymbol{G}^+(z), \tag{7}$$

where $\boldsymbol{G}^+(z) = \boldsymbol{G}(x) \times \boldsymbol{G}^*(y)$. When S and S^* are considered as systems involved in joint motion, such a separation into noninteracting systems becomes impossible. However, it is important that, as in the case of noninteracting systems, the invariant density of the combined system S^+ is the Cartesian product of the densities, $\sigma_\vartheta(x)$ and $\sigma^*_\vartheta(y)$,

$$\sigma^+_\vartheta(z) = \sigma_\vartheta(x) \times \sigma^*_\vartheta(y), \tag{8}$$

that is, the systems S and $\mathrm{S}^*$are statistically independent in the equilibrium state.

To design thermostats, we have to modify the equations of motion (7), under the assumption of ergodicity, in accordance with the dynamic principle [28], which requires the concept of temperature expressions.

3. Temperature expression

In this section, we explain theoretical details of the temperature expression concept.

Let the system S be in contact with the heat reservoir at temperature T, then we define the temperature expression associated with S system in terms of the system state variables $x \in \mathcal{M}$. Of course, the same definition applies to the system S^*, provided that it is not empty ($n^* \geq 1$), as well applied to the combined system S^+. In the case of empty S^* system, that is, $n^* = 0$, only stochastic thermostatted dynamics is possible.

The function of system state, $\Theta(x,\vartheta)$, $\Theta : \mathcal{M} \times \mathbb{R}_+ \to \mathbb{R}$, is called a temperature expression (in short, ϑ-expression) if it explicitly depends on the temperature ($\vartheta = k_B T$, where k_B is the Boltzmann constant) and satisfies the condition,

$$\int_{\mathcal{M}} \Theta(x,\vartheta) d\mu_\vartheta(x) = 0 \quad \text{for all} \quad \vartheta > 0, \tag{9}$$

where $d\mu_\vartheta(x) = \sigma_\vartheta(x)dx$ is the probability distribution as defined above.

Remark: We call Θ the temperature expression according to the initial manifestation of such a construction in statistical mechanics, where the parameter ϑ is the thermodynamic temperature, however, the ϑ can be understood in a broader sense, without linking its value to thermodynamic temperature.

The set of all ϑ-expressions for an arbitrary but fixed value of the ϑ-parameter is a linear system in which the operations of addition ϑ-expressions and multiplication ϑ-expressions by numbers are defined in the usual way. Indeed, it is easy to see from definition (9) that a linear combination of ϑ-expressions at a fixed value ϑ is again a ϑ-expression with the same value of ϑ.

For the purposes of study and use of the properties of ϑ-expressions, it will be necessary to interpret them as elements of either the space L_1 or L_2 (*e.g.,* [33]). This interpretation is appropriate here, since the ϑ-expressions we are considering are bounded from below and grow at infinity no faster than a polynomial.

For an arbitrary but fixed value of ϑ, L_1^ϑ denotes the set of all summable ϑ-expressions, $\Theta(x,\vartheta)$,

$$\int_{\mathcal{M}} |\Theta(x,\vartheta)| \, d\mu_\vartheta(x) < \infty.$$

L_1^ϑ is a normed linear space where norm is defined in the usual way

$$\|\Theta(x,\vartheta)\| = \int_{\mathcal{M}} |\Theta(x,\vartheta)| \, d\mu_\vartheta(x).$$

For an arbitrary but fixed value of ϑ, L_2^ϑ denotes the set of all square summable ϑ-expressions, $\Theta(x,\vartheta)$,

$$\int_{\mathcal{M}} (\Theta(x,\vartheta))^2 \, d\mu_\vartheta(x) < \infty.$$

L_2^ϑ is a linear Euclidean space with the scalar product,

$$(\Theta_1,\Theta_2) = \int_{\mathcal{M}} \Theta_1(x,\vartheta)\Theta_2(x,\vartheta) d\mu_\vartheta(x),$$

and the norm defined in the usual way,

$$\|\Theta(x,\vartheta)\| = \sqrt{(\Theta,\Theta)} = \sqrt{\int_{\mathcal{M}} (\Theta(x,\vartheta))^2 \, d\mu_\vartheta(x)}.$$

Similarly, for the system S^* a temperature expression, $\Theta^*(y,\vartheta)$, $y \in \mathcal{M}^* = \mathbb{R}^{n^*}$, satisfies the condition,

$$\int_{\mathcal{M}^*} \Theta^*(y,\vartheta) d\mu^*_\vartheta(y) = 0 \quad \text{for all} \quad \vartheta > 0, \tag{10}$$

where $d\mu^*_\vartheta(y) = \sigma^*_\vartheta(y)dy$, as well as for the combined system S^+ a temperature expression satisfied the condition,

$$\int_{\mathcal{M}^+} \Theta^+(z,\vartheta) d\mu^+_\vartheta(z) = \int_{\mathcal{M}^+} \Theta^+((x,y)\,,\vartheta) d\mu_\vartheta(x) d\mu^*_\vartheta(y) = 0 \quad \text{for all} \quad \vartheta > 0, \tag{11}$$

In the last case of the combined system S^+, provided that $\int_{\mathcal{M}} |\Theta^+(z,\vartheta)|\, d\mu_\vartheta(z) < \infty$, we find from Fubini's theorem that

$$\begin{aligned}
\int_{\mathcal{M}^+} \Theta^+(z,\vartheta) d\mu^+_\vartheta(z) &= \int_{\mathcal{M}^+} \Theta^+(z,\vartheta) d\mu_\vartheta(x) d\mu^*_\vartheta(y) \\
&= \int_{\mathcal{M}} \left(\int_{\mathcal{M}^*} \Theta^+(z,\vartheta) d\mu^*_\vartheta(y) \right) d\mu_\vartheta(x) = \int_{\mathcal{M}} \Theta(x,\vartheta) d\mu_\vartheta(x) \\
&= \int_{\mathcal{M}^*} \left(\int_{\mathcal{M}} \Theta^+(z,\vartheta) d\mu_\vartheta(x) \right) d\mu^*_\vartheta(y) = \int_{\mathcal{M}^*} \Theta^*(y,\vartheta) d\mu^*_\vartheta(y) \\
&= 0.
\end{aligned}$$

This means that

$$\int_{\mathcal{M}} \Theta^+(z,\vartheta) d\mu_\vartheta(x) = \Theta^*(y,\vartheta) \tag{12}$$

and

$$\int_{\mathcal{M}^*} \Theta^+(z,\vartheta) d\mu^*_\vartheta(y) = \Theta(x,\vartheta) \tag{13}$$

are ϑ-expressions as defined above. Here are some trivial but important examples of combined ϑ-expressions:

$$\begin{aligned}
\Theta^+(z,\vartheta) &= \Theta(x,\vartheta) + \Theta^*(y,\vartheta), \qquad (14) \\
\Theta^+(z,\vartheta) &= \Theta(x,\vartheta) \times \Theta^*(y,\vartheta). \qquad (15)
\end{aligned}$$

It should be clarified here that ϑ-expression (9), separately from the combined ϑ-expression, $\Theta^+(z,\vartheta)$, can be used to design a dynamic thermostat only if the system S^* is empty ($n^* = 0$). But in this case it is impossible to construct deterministic thermostat equations, and the dynamic equations will be stochastic by necessity [28]. Suppose that the system S^* is not empty ($n^* \geq 1$), then, in order to include in the dynamic equations the joint motion of S and S^* systems, the ϑ-expression $\Theta(x,\vartheta)$ should be understood in the sense of the relation (13). Similar arguments can be given for the ϑ-expression $\Theta^*(y,\vartheta)$ and relation (12).

3.1. Examples

Note that only a few specific ϑ-expressions have been used so far and described in the literature (*e.g.* [3–6]), namely kinetic, virial, configurational, and also the so-called generalized temperature expression, all of them are considered in the context of Hamiltonian dynamics and invariant canonical density, that is, $\mathcal{V}(x) = H(x)$, $\boldsymbol{G}(x) = \mathbf{J}\boldsymbol{\nabla} H(x)$, $H(x)$ is the Hamiltonian function, the phase space $\mathcal{M}$, $x \in \mathcal{M}$, is even-dimensional.

Consider a system of N particles and assume the Hamiltonian function, $H(x)$, in the natural form,

$$H(x) = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m_i} + V(q),$$

where $x = (p, q) \in \mathcal{M} = \mathbb{R}^{2\mathcal{N}}$ represents a point in the phase space $\mathcal{M}$, $p = \{\mathbf{p}_i\}$ are momentum variables and $q = \{\mathbf{q}_i\}$ are position variables, $\mathcal{N}$ is number of degrees of freedom. Then the above listed well-known and utilized in thermostats ϑ-expressions are:

The kinetic ϑ-expression,

$$\Theta_{\text{kin}}(x, \vartheta) = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{m_i} - \mathcal{N}\vartheta = \sum_{i=1}^{N} \left(\frac{\mathbf{p}_i^2}{m_i} - 3\vartheta \right) = \sum_{i=1}^{N} \Theta_{i,\text{kin}}(p, \vartheta),$$

which originates in the equipartition theorem of statistical mechanics.

The virial ϑ-expression,

$$\Theta_{\text{vir}}(x, \vartheta) = \sum_{i=1}^{N} \mathbf{q}_i \cdot \boldsymbol{\nabla}_{\mathbf{q}_i} V(q) - \mathcal{N}\vartheta = \sum_{i=1}^{N} \left(\mathbf{q}_i \cdot \boldsymbol{\nabla}_{\mathbf{q}_i} V(q) - 3\vartheta \right) = \sum_{i=1}^{N} \Theta_{i,\text{vir}}(q, \vartheta),$$

The quantity $\mathbb{V}(q) = \sum_{i=1}^{N} \mathbf{q}_i \cdot \boldsymbol{\nabla}_{\mathbf{q}_i} V(q)$, defines the virial of forces in the configuration $\{q\}$. The virial (Clausius) theorem establishes a correspondence between the time-averaged kinetic energy and virial.

The configurational ϑ-expression,

$$\Theta_{\text{conf}}(x, \vartheta) = \sum_{i=1}^{N} \left[(\boldsymbol{\nabla}_{\mathbf{q}_i} V(q))^2 - \vartheta \Delta_{\mathbf{q}_i} V(q) \right] = \sum_{i=1}^{N} \Theta_{i,\text{conf}}(q, \vartheta),$$

Generalized ϑ-expression,

$$\Theta_{\text{gen}}(x, \vartheta) = \boldsymbol{\varphi}(x) \cdot \boldsymbol{\nabla} H(x) - \vartheta \boldsymbol{\nabla} \cdot \boldsymbol{\varphi}(x), \tag{16}$$

where $\boldsymbol{\varphi}(x)$ is a vector field such that $|\boldsymbol{\varphi}(x)| \exp[-\beta H(x)] \to 0$ as $|x| \to \infty$.

Remark: The above examples are special cases of the latter one, depending on the form of $\boldsymbol{\varphi}(x)$.

The proof that $\Theta_{\text{kin}}(x, \vartheta)$, $\Theta_{\text{vir}}(x, \vartheta)$, $\Theta_{\text{conf}}(x, \vartheta)$, and $\Theta_{\text{gen}}(x, \vartheta)$ are ϑ-expressions is by direct calculation.

4. Advanced selection of ϑ-expressions

4.1. Preliminary notes

To construct a broader set of ϑ-expressions than the examples given, we will follow a pattern that can be interpreted as an inversion of the collocation scheme [34]. To illustrate the method, consider the problem of calculating the integral

$$I = \int_{x_1}^{x_2} F(x) \sigma(x) dx.$$

Suppose that $\sigma(x)$ satisfies a differential equation of the form

$$\frac{d}{dx} \sigma(x) = \lambda(x) \sigma(x),$$

where $\lambda(x)$ is a rather arbitrary function. Then the calculation of the integral I can be reduced to solving the following differential equation for the function $\varphi(x)$,

$$\frac{d}{dx}\varphi(x) + \lambda(x)\varphi(x) = F(x)\sigma(x),$$

so that we get

$$I = \varphi(x_2)\sigma(x_2) - \varphi(x_1)\sigma(x_1).$$

Assume $F(x)$ is a ϑ-expression, that is, $I = 0$, $\sigma(x) \propto \exp\left[-\vartheta^{-1}\mathcal{V}(x)\right]$, and $x_1 \to -\infty$, $x_2 \to +\infty$, then we arrive at the particular form of the function $F(x)$,

$$F(x) = \sigma^{-1}(x)\left(-\vartheta\frac{d}{dx}\right)\left[\varphi(x)\sigma(x)\right], \tag{17}$$

where $\varphi(x)$ is a function bounded from below and growing no faster than a polynomial, that is, $|\varphi(x)| \le c_1(\vartheta)\,|x|^{c_2}$, where $c_1 > 0$ and $c_2 > 0$.

Let us define now a set of ϑ-expressions, ω_n, based on the analogy with the definition of Hermite polynomials, that is, Rodrigues' type formula,

$$\omega_n(x,\vartheta) = \sigma_\vartheta^{-1}(x)\,(-\vartheta)^n\,\frac{d^n}{dx^n}\left[\sigma_\vartheta(x)\right] = \exp\left\{\vartheta^{-1}\mathcal{V}(x)\right\}(-\vartheta)^n\,\frac{d^n}{dx^n}\left[\exp\left\{-\vartheta^{-1}\mathcal{V}(x)\right\}\right], \tag{18}$$

where $n \ge 1$. $\omega_n(x,\vartheta)$ is a polynomial of degree n in ϑ. The Hermite polynomials, both univariate and multivariate, were introduced in [35, 36] and reproduced in [37, 38]. We use the probabilistic definition of Hermite polynomials, which are often called Chebyshev-Hermite (or Tchebychef-Hermite) polynomials [35, 37, 39–41]. These polynomials are closely related to the normal probability distribution and are widely used in the theory of probability and random processes. In what follows, we are mainly interesting in multivariate ϑ-expressions, and will follow the analogy with multivariate Chebyshev–Hermite polynomials, as described in article [42].

The generating function of ϑ-expressions ω_n has the form

$$\begin{aligned}
\Phi_\omega(h;x) &= \sum_{n=0}^{\infty}\frac{1}{n!}\omega_n\left(x,\vartheta\right)\left(\frac{h}{\vartheta}\right)^n \\
&= \exp\left\{\vartheta^{-1}\mathcal{V}(x)\right\}\sum_{n=0}^{\infty}\frac{1}{n!}\left(-h\frac{d}{dx}\right)^n\left[\exp\left\{-\vartheta^{-1}\mathcal{V}(x)\right\}\right] \\
&= \exp\left\{-\vartheta^{-1}\left[\mathcal{V}(x-h) - \mathcal{V}(x)\right]\right\},
\end{aligned}$$

where we formally add the value $\omega_0 = 1$ (considering that this is not a ϑ-expression). It should also be noted that the expression $\omega_1\left(x,\vartheta\right) = \mathcal{V}'(x)$ does not explicitly depend on ϑ and therefore does not satisfy the condition to be ϑ-expression, but all $\{\omega_n(x,\vartheta)\}_{n\ge 2}$ are ϑ-expressions.

The following recurrent relation can be easily obtained from the definition,

$$\omega_{n+1}(x,\vartheta) = \left(\frac{d}{dx}\mathcal{V}(x)\right)\omega_n(x,\vartheta) - \vartheta\frac{d}{dx}\omega_n(x,\vartheta). \tag{19}$$

For lower-order expressions, we explicitly obtain the following formulas,

$$\omega_1\left(x,\vartheta\right) = \mathcal{V}'(x), \tag{20a}$$

$$\omega_2\left(x,\vartheta\right) = \left(\mathcal{V}'(x)\right)^2 - \vartheta\mathcal{V}''(x), \tag{20b}$$

$$\omega_3\left(x,\vartheta\right) = \left(V'(x)\right)^3 - 3\vartheta\mathcal{V}''(x)\mathcal{V}'(x) + \vartheta^2\mathcal{V}'''(x), \tag{20c}$$

$$\omega_4\left(x,\vartheta\right) = \left(V'(x)\right)^4 - 6\vartheta\mathcal{V}''(x)\left(\mathcal{V}'(x)\right)^2 + \vartheta^2\left[4\mathcal{V}'(x)\mathcal{V}'''(x) + 3\left(\mathcal{V}''(x)\right)^2\right] - \vartheta^3\mathcal{V}^{(4)}(x), \tag{20d}$$

and so forth, where we used the notation,

$$\frac{d}{dx}\mathcal{V}(x) \equiv \mathcal{V}'(x), \quad \frac{d^2}{dx^2}\mathcal{V}(x) \equiv \mathcal{V}''(x), \quad \cdots, \quad \frac{d^n}{dx^n}\mathcal{V}(x) \equiv \mathcal{V}^{(n)}(x), \quad \cdots \quad .$$

Following the main line defined by formula (17) let us consider the generalized expression depending on a function $\varphi(x, \vartheta)$ (dependence on ϑ is optional) bounded from below and growing no faster than a polynomial

$$\begin{aligned} \Omega_n(x, \vartheta) &= \sigma_\vartheta^{-1}(x)\,(-\vartheta)^n \frac{d^n}{dx^n}\left[\varphi(x,\vartheta)\sigma_\vartheta(x)\right] \\ &= \exp\left\{\vartheta^{-1}\mathcal{V}(x)\right\}(-\vartheta)^n \frac{d^n}{dx^n}\left[\varphi(x,\vartheta)\exp\left\{-\vartheta^{-1}\mathcal{V}(x)\right\}\right], \end{aligned} \tag{21}$$

together with the corresponding generating function,

$$\begin{aligned} \Phi_\Omega(h;x) &= \sum_{n=0}^{\infty} \frac{1}{n!}\Omega_n(x,\vartheta)\left(\frac{h}{\vartheta}\right)^n \\ &= \exp\left\{\vartheta^{-1}\mathcal{V}(x)\right\}\sum_{n=0}^{\infty}\frac{1}{n!}\left(-h\frac{d}{dx}\right)^n\left[\varphi(x,\vartheta)\exp\left\{-\vartheta^{-1}\mathcal{V}(x)\right\}\right] \\ &= \varphi(x-h,\vartheta)\exp\left\{-\vartheta^{-1}\left[\mathcal{V}(x-h)-\mathcal{V}(x)\right]\right\}, \end{aligned}$$

The following recurrent relation can be easily obtained from the definition of the set of ϑ-expressions, $\{\Omega_n(x,\vartheta)\}_{n\in\mathbb{N}_0}$, where $\Omega_0(x,\vartheta) = \varphi(x,\vartheta)$,

$$\Omega_{n+1}(x,\vartheta) = \left(\frac{d}{dx}\mathcal{V}(x)\right)\Omega_n(x,\vartheta) - \vartheta\frac{d}{dx}\Omega_n(x,\vartheta). \tag{22}$$

For lower-order expressions we explicitly obtain,

$$\Omega_0(x,\vartheta) = \varphi(x,\vartheta), \tag{23a}$$

$$\Omega_1(x,\vartheta) = \varphi(x,\vartheta)\mathcal{V}'(x) - \vartheta\varphi'(x,\vartheta), \tag{23b}$$

$$\Omega_2(x,\vartheta) = \varphi(x,\vartheta)\left(\mathcal{V}'(x)\right)^2 - \vartheta\left[2\varphi'(x,\vartheta)\mathcal{V}'(x) + \varphi(x,\vartheta)\mathcal{V}''(x)\right] + \vartheta^2\varphi''(x,\vartheta), \tag{23c}$$

$$\begin{aligned} \Omega_3(x,\vartheta) &= \varphi(x,\vartheta)\left(\mathcal{V}'(x)\right)^2 - \vartheta\left[3\varphi'(x,\vartheta)\left(\mathcal{V}'(x)\right)^2 + 3\varphi(x,\vartheta)\mathcal{V}'(x)\mathcal{V}''(x)\right] \\ &\quad + \vartheta^2\left[3\varphi''(x,\vartheta)\mathcal{V}'(x) + \varphi(x,\vartheta)\mathcal{V}'''(x)\right] - \vartheta^3\varphi'''(x,\vartheta), \end{aligned} \tag{23d}$$

and so forth.

Note that the expression $\Omega_0(x,\vartheta)$ is a ϑ-expression only if $\varphi(x,\vartheta)$, in turn, is a ϑ-expression.

4.2. Other options

In a general setting, the problem is to construct sets of ϑ-expressions in the form of polynomials in ϑ. It is expected that as the power of ϑ increases, the corresponding ϑ-expression will contain increasingly detailed statistical information about the phase variables and their functions.

Alternative procedure for generating meaningful sets of ϑ-expressions can be formulated as follows. Consider a set of ϑ-expressions, $\{\mathit{\Omega}_n(x,\vartheta)\}_{n\in\mathbb{N}_0}$, as a mapping of suitable functions $\{\varphi_n(x,\vartheta)\}_{n\in\mathbb{N}_0}$, keeping only the first derivative with respect to the variable x,

$$\begin{aligned} \mathit{\Omega}_n(x,\vartheta) &= \sigma_\vartheta^{-1}(x)\left(-\vartheta\frac{d}{dx}\right)\left[\varphi_n(x,\vartheta)\sigma_\vartheta(x)\right] \\ &= -\vartheta\exp\left\{\vartheta^{-1}\mathcal{V}(x)\right\}\frac{d}{dx}\left[\varphi_n(x,\vartheta)\exp\left\{-\vartheta^{-1}\mathcal{V}(x)\right\}\right] \\ &= \left[\mathcal{V}'(x) - \vartheta\frac{d}{dx}\right]\varphi_n(x,\vartheta). \end{aligned} \tag{24}$$

Then the set $\{\Omega_n(x,\vartheta)\}_{n\in\mathbb{N}_0}$ of ϑ-expressions can be generated from a set $\{\varphi_n(x,\vartheta)\}_{n\in\mathbb{N}_0}$ of suitable polynomials of order n in ϑ by the relationship (24). Let us consider a few supporting examples.

4.2.1. Consider the Chebyshev-Hermite polynomials with the parameter ϑ [37, 41], $He_n\left(x;\vartheta\right)$, $n\in\mathbb{N}_0$, as functions $\varphi_n(x,\vartheta)$, that is, explicitly,

$$\varphi_n(x,\vartheta)=He_n(x;\vartheta)=\frac{(-\vartheta)^n}{n!}\exp\left(\frac{x^2}{2\vartheta}\right)\frac{d^n}{dx^n}\left[\exp\left(-\frac{x^2}{2\vartheta}\right)\right],\quad n\in\mathbb{N}_0.$$

Then we arrive at the following set of ϑ-expressions as polynomials in ϑ of order n,

$$\Omega_n(x,\vartheta)=\mathcal{V}'(x)He_n(x;\vartheta)-\vartheta He_{n-1}(x;\vartheta),$$

where the relationship

$$\frac{d}{dx}He_n(x;\vartheta)=He_{n-1}(x;\vartheta) \tag{25}$$

was used. We set $He_{-1}(x;\vartheta)=0$ and $He_0(x;\vartheta)=1$. The set of functions

$$\psi_n(x,\vartheta)=\sqrt{\frac{n!}{\vartheta^n}}He_n(x;\vartheta),\quad n\in\mathbb{N}_0$$

is the complete orthonormal system in $L_2\left(\mathbb{R},d\mu(x)\right)$, where

$$d\mu(x)=\exp\left(-\frac{x^2}{2\vartheta}\right)\frac{dx}{\sqrt{2\pi\vartheta}}dx.$$

It is worth noting that $He_n(x;\vartheta)$ themselves are not really ϑ-expressions for the density $\sigma_\vartheta(x)$.

As a result, we conclude that a ϑ-expression Ω can be expressed as

$$\Omega(x,\vartheta)=\sum_{n=0}^{\infty}a_n\left(\vartheta\right)\left[\mathcal{V}'(x)-\vartheta\frac{d}{dx}\right]He_n(x;\vartheta)=\sum_{n=0}^{\infty}a_n\left(\vartheta\right)\Omega_n(x,\vartheta),$$

where $\{a_n\left(\vartheta\right)\}_{n=0}^{\infty}$ are expansion coefficients of a ϑ-expression.

4.2.2. Let us take the set $\{\omega_n(x,\vartheta)\}_{n\in\mathbb{N}}$ of ϑ-expressions (19) as functions $\varphi_n(x,\vartheta)$ in equation (24). Then we arrive at the following result

$$\begin{aligned}\Omega_n(x,\vartheta)&=-\vartheta\exp\left\{\vartheta^{-1}\mathcal{V}(x)\right\}\frac{d}{dx}\left[\omega_n(x,\vartheta)\exp\left\{-\vartheta^{-1}\mathcal{V}(x)\right\}\right]\\&=\left[\mathcal{V}'(x)-\vartheta\frac{d}{dx}\right]\omega_n(x,\vartheta)=\omega_{n+1}(x,\vartheta).\end{aligned}$$

Thus, this particular scheme does not result in a new set of ϑ-expressions. However, this was to be expected.

4.2.3. In this subsection, we associate the construction of ϑ-expressions with the classical Appell sequences. The set $\{\varphi_n(x)\}$ is an Appell sequence [43, 44] if the following relation holds

$$\frac{d}{dx}\varphi_n(x) = \varphi_{n-1}(x), \quad n \in \mathbb{N}.$$

The Chebyshev-Hermite polynomials have this property, as indicated by the relationship (25), and thus are an Appell sequence. The property of the set $\{\varphi_n(x)\}$ to be a sequence of Appell polynomials with the parameter ϑ is typical for our purposes. In this regard, let us recall some well-known facts about Appell sequences [43, 44].

Let $\{\varphi_n(x)\}_{n\in\mathbb{N}_0}$ be an Appell sequence, then between this sequence and a sequence of numbers $\{a_k\}_{k\in\mathbb{N}_0}$, where $a_0 \neq 0$, there exists the one-to-one correspondence,

$$\varphi_n(x) = a_0\frac{x^n}{n!} + a_1\frac{x^{n-1}}{(n-1)!} + \cdots + a_n\frac{x^0}{0!} = \sum_{k=0}^{n} a_k\frac{x^{n-k}}{(n-k)!}.$$

In a form convenient for us: A necessary and sufficient condition for $\{\varphi_n(x)\}_{n\in\mathbb{N}_0}$ to be an Appell sequence is that there exists a power series

$$\chi(s) = \sum_{n=0}^{\infty} a_n s^n$$

such that

$$\exp(sx)\,\chi(s) = \sum_{n=0}^{\infty} \varphi_n(x)s^n.$$

The power series $\chi(s)$ is called the generating function for the sequence $\{\varphi_n(x)\}$. The generating function is defined as a formal series which allows operations of differentiation, taking the logarithm, exponentiation, and others. Equality of two formal power series means equality of their corresponding coefficients.

To establish a relationship between Appell polynomials and ϑ-expressions, consider a probability density $\sigma_\vartheta(x) \propto \exp\left[-\vartheta^{-1}V(x)\right]$, where $V(x)$ is a suitable coercive function, and define two characteristic functions, $\mathscr{M}(s;\vartheta)$ and $\mathscr{K}(s;\vartheta)$, such that they are generating functions for moments and cumulants, that is,

$$\mathscr{M}(s;\vartheta) = \mathbb{E}_\vartheta\{\exp(sx)\} = \sum_{n=0}^{\infty}\frac{1}{n!}\mu_n(\vartheta)\,s^n,$$

where n-th moment of the variable x with density $\sigma_\vartheta(x)$ is

$$\mu_n(\vartheta) = \mathbb{E}_\vartheta\{x^n\} = \int x^n\sigma_\vartheta(x)dx, \quad n \in \mathbb{N}_0.$$

The cumulants $\kappa_n(\vartheta)$ are defined by the cumulant generating function, $\mathscr{K}(s;\vartheta)$, as follows

$$\mathscr{K}(s;\vartheta) = \ln\mathscr{M}(s;\vartheta) = \sum_{n=0}^{\infty}\frac{1}{n!}\kappa_n(\vartheta)\,s^n, \quad n \in \mathbb{N}_0.$$

Cumulants and moments are connected by the formal relationship between coefficients in the Taylor expansion of $\mathscr{M}(s;\vartheta)$ and $\mathscr{K}(s;\vartheta)$. This relationship can be obtained in explicit form based on the Faà di Bruno formula [45]. For the first cumulants, it turns out the familiar relationships,

$$\begin{aligned}
&\kappa_0(\vartheta) = 0, \\
&\kappa_1(\vartheta) = \mu_1(\vartheta), \\
&\kappa_2(\vartheta) = \mu_2(\vartheta) - \mu_1^2(\vartheta), \\
&\kappa_3(\vartheta) = \mu_3(\vartheta) - 3\mu_2(\vartheta)\mu_1(\vartheta) + 2\mu_1^3(\vartheta),
\end{aligned}$$

and so forth.

In fact, cumulants are very useful tool for the purposes of statistical analysis of both stochastic and deterministic dynamical systems [46–48]. In this regard, it should be recalled that the Gaussian probability density has a cumulant generating function in the form of a quadratic polynomial. According to Marcinkiewicz's theorem [45, 49], this is the only probability density that has a finite number of nonzero cumulants. In other words, if $\mathscr{K}_n(s)$ is a polynomial of degree $n > 2$ then $\mathscr{M}(s) = \exp\{\mathscr{K}_n(s)\}$ can not be a characteristic function.

In context of statistical ensemble control tools (thermostats), cumulant analysis is also useful, as has recently been demonstrated [24, 50].

Let us now consider the sequence of Appell polynomials, $\varphi_n(x;\vartheta)$, such that the corresponding generating function has the form,

$$\chi(s;\vartheta) = \exp\left[-\mathscr{K}(s;\vartheta)\right],$$

so that

$$\sum_{n=0}^{\infty} \varphi_n(x;\vartheta)s^n = \exp\left[sx - \mathscr{K}(s;\vartheta)\right].$$

In the case of the Gaussian probability density function, that is,

$$\sigma_\vartheta(x) \propto \exp\left(-\frac{x^2}{2\vartheta}\right),$$

so that

$$\mathscr{K}(s;\vartheta) = \exp\left(\frac{1}{2}\vartheta s^2\right),$$

we arrive at the Chebyshev-Hermite polynomials with parameter ϑ,

$$\sum_{n=0}^{\infty} \varphi_n(x;\vartheta)s^n = \exp\left[sx - \frac{1}{2}\vartheta s^2\right] = \sum_{n=0}^{\infty} He_n(x;\vartheta)s^n.$$

Let us note the possibility of investigating, in line with the topic of this work, other well-known Appell sequences, namely the famous Bernoulli and Euler polynomials.

4.2.4. Consider the well-known Appell sequence, namely,

$$\left\{\frac{1}{n!}x^n\right\}_{n\in\mathbb{N}_0}.$$

This sequence does not depend on the parameter ϑ. Therefore, for our purposes, a generating function of the following form will be more suitable,

$$\chi(s) = \exp\left(-a\vartheta s\right),$$

where a is a parameter. In this case,

$$\exp\left[sx - a\vartheta s\right] = \sum_{n=0}^{\infty} \varphi_n(x;\vartheta)s^n,$$

and we arrive at an Appell sequence of the form

$$\varphi_n(x;\vartheta) = \frac{1}{n!}\left(x - a\vartheta\right)^n, \quad n \in \mathbb{N}_0.$$

This Appell sequence can be used in the same way as other ϑ-expressions. For example, as the following sequence,

$$\Omega_n(x,\vartheta) = \left[\mathcal{V}'(x) - \vartheta\frac{d}{dx}\right]\frac{1}{n!}\left(x - a\vartheta\right)^n, \quad n \in \mathbb{N}_0.$$

4.2.5. To complete this Section, consider a sequence of ϑ-expressions defined by successive iterations of a given function, $\phi(x,\vartheta)$. This function may or may not be a ϑ-expression. Explicitly,

$$\begin{aligned}
\Omega_1(x,\vartheta) &= -\vartheta\exp\left\{\vartheta^{-1}\mathcal{V}(x)\right\}\frac{d}{dx}\left[\phi(x,\vartheta)\exp\left\{-\vartheta^{-1}\mathcal{V}(x)\right\}\right] \\
&= \left[\mathcal{V}'(x) - \vartheta\frac{d}{dx}\right]\phi(x,\vartheta), \\
\Omega_2(x,\vartheta) &= -\vartheta\exp\left\{\vartheta^{-1}\mathcal{V}(x)\right\}\frac{d}{dx}\left[\Omega_1(x,\vartheta)\exp\left\{-\vartheta^{-1}\mathcal{V}(x)\right\}\right] \\
&= \left[\mathcal{V}'(x) - \vartheta\frac{d}{dx}\right]\Omega_1(x,\vartheta) = \left[\mathcal{V}'(x) - \vartheta\frac{d}{dx}\right]^2\phi(x,\vartheta),
\end{aligned}$$

and so forth.

Thus, we arrive at the following sequence of ϑ-expressions,

$$\Omega_n(x,\vartheta) = \left[\mathcal{V}'(x) - \vartheta\frac{d}{dx}\right]^n\phi(x,\vartheta), \quad n \in \mathbb{N}.$$

Taking into account the previously obtained recurrent relation (22), we arrive at the useful formula,

$$\Omega_n(x,\vartheta) = \exp\left\{\frac{1}{\vartheta}\mathcal{V}(x)\right\}(-\vartheta)^n\frac{d^n}{dx^n}\left[\phi(x,\vartheta)\exp\left\{-\frac{1}{\vartheta}\mathcal{V}(x)\right\}\right] = \left[\mathcal{V}'(x) - \vartheta\frac{d}{dx}\right]^n\phi(x,\vartheta), \quad (26)$$

where $\Omega_0(x,\vartheta) = \phi(x,\vartheta)$, so we set $n \in \mathbb{N}_0$. As stated earlier, the function $\phi(x,\vartheta)$ may or may not be a ϑ-expression.

We present explicit formulas for special cases, namely, $\phi(x,\vartheta) = 1$ and $\mathcal{V}(x) = \frac{1}{2}x^2$,

$$\omega_n(x,\vartheta) = \exp\left\{\frac{1}{\vartheta}\mathcal{V}(x)\right\}(-\vartheta)^n\frac{d^n}{dx^n}\exp\left\{-\frac{1}{\vartheta}\mathcal{V}(x)\right\} = \left[\mathcal{V}'(x) - \vartheta\frac{d}{dx}\right]^n 1,$$

$$He_n(x;\vartheta) = \frac{1}{n!}\exp\left(\frac{x^2}{2\vartheta}\right)(-\vartheta)^n\frac{d^n}{dx^n}\left[\exp\left(-\frac{x^2}{2\vartheta}\right)\right] = \frac{1}{n!}\left[x - \vartheta\frac{d}{dx}\right]^n 1.$$

In the multivariate case, it is necessary to take into account the commutativity property of the corresponding differential operators.

Also, as a result of summation of ϑ-expressions, we obtain

$$\Omega(x,\vartheta) = -1 + \sum_{n=0}^{\infty} \frac{1}{n!}\left[\mathcal{V}'(x) - \vartheta\frac{d}{dx}\right]^n \phi(x,\vartheta) = -1 + \exp\left\{\mathcal{V}'(x) - \vartheta\frac{d}{dx}\right\}\phi(x,\vartheta).$$

In such context

$$\Omega_n(x,\vartheta) = -1 + \exp\left\{\mathcal{V}'(x) - \vartheta\frac{d}{dx}\right\}\frac{1}{n!}x^n.$$

4.2.6. Let us take $\phi(x,\vartheta) = \mathcal{V}'(x)$. Then we have $\mathbb{E}_\vartheta\left\{\mathcal{V}'(x)\right\} = 0$ and thus we arrive at the following sequence of ϑ-expressions,

$$\begin{aligned}
\Omega_0(x,\vartheta) &= \mathcal{V}'(x),\\
\Omega_1(x,\vartheta) &= \left(\mathcal{V}'(x)\right)^2 - \vartheta\mathcal{V}''(x),\\
\Omega_2(x,\vartheta) &= \left(\mathcal{V}'(x)\right)^3 - \vartheta\left[2\left(\mathcal{V}'(x)\right) + \mathcal{V}'(x)\mathcal{V}''(x)\right] + \vartheta^2\mathcal{V}'''(x),
\end{aligned}$$

and so forth. Thus, all ϑ-expressions are expressed exclusively in terms of the function $\mathcal{V}(x)$.

5. Multivariate case

This case will be discussed in detail elsewhere. Here, let us just touch on this case.

We utilize the multi-index notation as described in [51]. Multi-index m is a set (vector) $m = (m_1, m_2, ..., m_n)$, where $m_i \in \mathbb{N}_0$, that is, $\{m_i\}$ are non-negative integers. Let m be a multi-index, then

$$|m| = m_1 + m_2 + \ldots + m_n, \qquad m! = m_1!m_2!\ldots m_n!, \qquad \boldsymbol{\varphi}^{\cancel{m}}(x) = \varphi_1^{\cancel{m}_1}(x)\,\varphi_2^{\cancel{m}_2}(x)\ldots\varphi_n^{\cancel{m}_n}(x)\,,$$

where $\boldsymbol{\varphi}(x) = (\varphi_1(x), \varphi_2(x), \ldots, \varphi_n(x))$ is a vector field, $\cancel{m}_i = 0$ if $m_i = 0$, $\cancel{m}_i = 1$ if $m_i \geq 1$. Concerning multi-index derivatives we set

$$\partial = (\partial_1, \partial_2, \ldots, \partial_n)\,, \quad \partial^m = \partial_1^{m_1}\partial_2^{m_2}, \ldots, \partial_n^{m_n}; \quad D_i \equiv -\vartheta\partial_i; \quad D^m = (-\vartheta)^{|m|}\,\partial^m.$$

Let us define ϑ-expressions constructively, similar to the univariate case,

$$\Theta_m(x,\theta) = \exp\left\{\vartheta^{-1}\mathcal{V}(x)\right\} D^m \cdot \left[\boldsymbol{\varphi}^{\cancel{m}}(x,\vartheta)\exp\left\{-\vartheta^{-1}\mathcal{V}(x)\right\}\right], \tag{27}$$

where $|m| \geq 1$, dot denotes component-wise multiplication of vectors, and the vector field $\boldsymbol{\varphi}(x,\vartheta)$ satisfies some integrability conditions so that equation (9) is valid. Dependence of $\boldsymbol{\varphi}(x,\vartheta)$ on ϑ is optional.

Let us consider the sum over all solutions of the Diophantine equation $m_1 + m_2 + \ldots + m_n = 1$,

$$\Theta^{(1)}(x,\theta) = \sum_{|m|=1}\Theta_m(x,\theta). \tag{28}$$

In virtue of the equality,

$$\exp\left\{\vartheta^{-1}\mathcal{V}(x)\right\}(-\vartheta\partial_i)\left(\varphi_i(x,\vartheta)\exp\left\{-\vartheta^{-1}\mathcal{V}(x)\right\}\right) = \varphi_i(x,\vartheta)\,\partial_i\mathcal{V}(x) - \vartheta\partial_i\varphi_i(x,\vartheta)\,,$$

where $i = 1, 2, \ldots, n$, we can rewrite the expression (28) as

$$\Theta^{(1)}(x,\vartheta) = \boldsymbol{\varphi}(x,\vartheta)\cdot\boldsymbol{\nabla}_x\mathcal{V}(x) - \vartheta\boldsymbol{\nabla}_x\cdot\boldsymbol{\varphi}(x,\vartheta), \tag{29}$$

so that this expression obviously includes the ϑ-expression $\Theta_{\text{gen}}(x,\theta)$ (16) as a special case. Note that the usual $\Theta_{\text{gen}}(x,\theta)$ involves a vector field $\boldsymbol{\varphi}(x)$, which is independent of ϑ. However, assuming dependence on ϑ and treating $\boldsymbol{\varphi}(x,\vartheta)$ as a vector with ϑ-expression components, we arrive at extremely rich thermostatted dynamics and expect a better control of the desired statistical properties of certain thermostats.

Just for example, let the vector field $\boldsymbol{\varphi}(x,\vartheta)$ in the ϑ-expression (29) be

$$\boldsymbol{\varphi}(x,\vartheta) = \boldsymbol{\psi}(x,\vartheta) \circ \boldsymbol{\nabla}_x \mathcal{V}(x) - \vartheta \boldsymbol{\nabla}_x \circ \boldsymbol{\psi}(x,\vartheta),$$

that is, a vector constructed from some ϑ-expression, where "$\circ$" denotes the component-wise (Hadamard) product of two vectors and dependence of a vector field $\boldsymbol{\psi}(x,\vartheta)$ on ϑ is optional. Thus, we arrive at the ϑ-expression, $\Theta^{(2)}(x,\vartheta)$, which is of higher order in ϑ

$$\begin{aligned}\Theta^{(2)}(x,\vartheta) = &\Big(\boldsymbol{\psi}(x,\vartheta) \circ \boldsymbol{\nabla}_x \mathcal{V}(x) - \vartheta \boldsymbol{\nabla}_x \circ \boldsymbol{\psi}(x,\vartheta)\Big) \cdot \boldsymbol{\nabla}_x \mathcal{V}(x) \\ &- \vartheta \boldsymbol{\nabla}_x \cdot \Big(\boldsymbol{\psi}(x,\vartheta) \circ \boldsymbol{\nabla}_x \mathcal{V}(x) - \vartheta \boldsymbol{\nabla}_x \circ \boldsymbol{\psi}(x,\vartheta)\Big).\end{aligned}$$

The described procedure can be repeated as needed. Case $|m| = 1$ is the most common in the literature, but higher order polynomials are also found, for example [28].

6. Conclusion

We have presented a new method for generating a wide variety of increasingly complex microscopic temperature expressions in the form of functional polynomials in thermodynamic temperature. This method is applicable to the case of arbitrary probability measures. The connection of proposed polynomials with classical special functions, in particular, with the Appell sequences, is revealed. To outline the main points of our method, we focused on the univariate case and only briefly touched on the multivariate case, which will be discussed in detail elsewhere.

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