



## Temperature Expressions and Thermostats

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**Abstract.** Molecular dynamics (MD) simulations are performed under certain thermodynamic conditions, typically at fixed temperature and pressure. The thermodynamic variables in the MD are modeled using equations that are called thermostats. Many different thermostats, deterministic and stochastic, have been proposed. In this presentation, we offer an extended set of microscopic temperature expressions, which includes expressions known in the literature as a special case, and also investigate some of their properties. Then we focused on a particular, but important case of mapping a vector of temperature expressions to temperature expressions. We expect that the latter result can be used to improve the schemes of well-known thermostats with minimal computational costs.

### 1. Introduction

Molecular dynamics (MD) [1–4] is an inevitable companion of research in a range of disciplines in natural sciences including such branches as the design of new functional materials and the drug discovery. MD simulation (similar to laboratory experiments) is performed under certain (thermodynamic) environmental conditions, usually at fixed temperature and pressure. For example, in order to implement the condition of constant ambient temperature in the equations of motion of a physical system, first of all, it is necessary to formulate some expression of temperature in terms of dynamic variables so that this expression plays the role of a dynamic temperature regulator in the evolution of a physical system. The reliability of using the concept of temperature expression is based on the ergodic hypothesis. This hypothesis equates the long-run time average of a physical observable to its ensemble average. Although deterministic thermostats are known to often violate ergodicity, *e.g.*, [5–7], they are assumed to be useful for practical purposes. At the same time, the ergodicity of stochastic thermostats, for which rigorous [8] results were obtained, seems to be a very probable property.

The concept of thermodynamic temperature is phenomenological. At the same time, dynamic temperature control tools must measure temperature as an average over time. Thus, we need a function of dynamic variables such that, under the assumption of ergodicity, the temperature can be expressed by averaging of this function over time along the trajectory in the phase space of the system. However, there is no any unique function of dynamic variables corresponding to the thermodynamic temperature, and the microscopic temperature expression can take alternative forms. Some early and well-known approaches to establishing the relationship between temperature and dynamics will be described in Section 3. In this regard, it is not surprising that various dynamic temperature control tools 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, 8–11].

Previously, we have shown that a range of thermostats can be derived in the framework of a unified approach based on the fundamental principles of statistical physics [12]. However, in order to demonstrate the relationship with previously proposed thermostats, this result was presented in the context of a limited set of temperature expressions. At the same time, the advantages of the unified method [12] for constructing thermostats have partially remained in the shadows and may not seem obvious from the point of view both mathematical theory and practical use.

Our goal here is to formulate a wider range of temperature expressions as well as to study their properties and potential for practical application.

## 2. Brief description of the temperature control concept

The design of dynamic thermostats is based on the concept of temperature expression [12]. Let us briefly recall the details of corresponding theoretical scheme, which are essential for this article.

It is assumed that the physical system of interest to us,  $S$ , placed in the thermal reservoir,  $\Sigma$ , (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 undisturbed part of the heat reservoir  $\Sigma \setminus S^*$  can fluctuate, while the temperature of reservoir  $\Sigma \setminus S^*$  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,  $\Sigma \setminus S^*$ , 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 this additional degrees of freedom is as important as the kinetic energy control of the  $S$  system. 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  $\sigma_{\vartheta}(x) \propto \exp\{-\vartheta^{-1}\mathcal{V}(x)\}$ ,  $x \in \mathcal{M} = \mathbb{R}^n$  (the phase space is not necessarily even dimensional), so that  $\mathcal{V}(x) : \mathcal{M} \rightarrow \mathbb{R}$ ,  $\mathcal{V}(x) = -\vartheta \ln \sigma(x)$ , where  $\vartheta > 0$  is a parameter. Consider a pair of vector fields, the potential  $\nabla\mathcal{V}(x)$  and incompressible  $\mathbf{G}(x)$ , that is,  $\nabla \cdot \mathbf{G}(x) = 0$  for all  $x \in \mathcal{M}$ , such that  $\nabla\mathcal{V}(x) \cdot \mathbf{G}(x) = 0$  for all  $x \in \mathcal{M}$  (in other words,  $\nabla\mathcal{V}(x)$  and  $\mathbf{G}(x)$  form a cosymmetric pair [13]). Then we associate with the system  $S$  the equations of motion,

$$\dot{x} = \mathbf{G}(x). \quad (1)$$

Thus, we arrive at the following properties,  $\dot{\mathcal{V}} = \nabla\mathcal{V}(x) \cdot \mathbf{G}(x) = 0$  and  $\nabla \cdot (\mathbf{G}(x) \sigma(x)) = 0$ , that is,  $\mathcal{V}(x)$  is a first integral and the density  $\sigma(x)$  is invariant for the dynamics (1).

Examples of cosymmetric pairs  $(\mathbf{G}(x), \nabla\mathcal{V}(x))$  include, but are not limited to:

- (i)  $\mathbf{G}(x) = \mathbf{0}$  (trivial case)
- (ii)  $\mathbf{G}(x) = \mathbf{\Lambda} \nabla\mathcal{V}(x)$ , where  $\mathbf{\Lambda}$  is an antisymmetric constant matrix; a particular case is  $\mathbf{\Lambda} = \mathbf{J}$  (symplectic unit), that is, the Hamiltonian system in even-dimensional phase space;
- (iii)  $\mathbf{G}(x) = \mathbf{A}(x) \nabla\mathcal{V}(x)$ , where  $\mathbf{A}(x)$  is a linear antisymmetric operator (matrix) depending on  $x$ ; a particular case is an antisymmetric operator  $\mathbf{A}(x)$  satisfying the Jacobi identity, that is, the Poisson system.

In all these cases, the vector fields are incompressible.

To design thermostats, we have to modify the equations of motion (1), under the assumption of ergodicity, in accordance with the dynamic principle [12], which first of all requires the definition of the concept of temperature expression.

### 3. Temperature expressions

Let the system S be in contact with the heat reservoir at temperature  $T$ , then we define the temperature expression in terms of the system state variables  $x \in \mathcal{M}$ . The same applies to the system  $S^*$ , provided that this system is not empty.

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

$$\int_{\mathcal{M}} \Theta(x, \vartheta) d\mu_{\vartheta}(x) = 0 \quad \text{for all } \vartheta > 0, \quad (2)$$

where  $d\mu_{\vartheta}(x) = \sigma_{\vartheta}(x)dx$ , is the probability distribution.

Similarly, for the  $S^*$  system  $\int_{\mathcal{M}^*} \Theta^*(y, \vartheta) d\mu_{\vartheta}^*(y) = 0$  for all  $\vartheta > 0$ , where  $d\mu_{\vartheta}^*(y) \propto \exp\{-\vartheta^{-1}\mathcal{V}^*(y)\}dy$ ,  $y \in \mathcal{M}^* = \mathbb{R}^{n^*}$ .

The useability of the temperature expression notion is based on the ergodic hypothesis, as well as the general concept of the dynamic ensemble control tools.

The ergodic hypothesis implies that for invariant densities

$$\lim_{\tau \rightarrow \infty} \frac{1}{\tau} \int_0^{\tau} \Theta(x(t), \vartheta) dt = 0 \quad (3)$$

for almost all trajectories. Similarly,  $\lim_{\tau \rightarrow \infty} \frac{1}{\tau} \int_0^{\tau} \Theta^*(y(t), \vartheta) dt = 0$ .

Let the  $\vartheta$ -expression  $\Theta(x, \vartheta)$ ,  $x \in \mathcal{M}$ , be given, then we modify the dynamical equations (1), under the assumption of ergodicity, in accordance with the requirement [12],

$$\nabla_x \mathcal{V}(x) \cdot \mathbf{G}(x) \propto \Theta(x, \vartheta). \quad (4)$$

Let us point out that it is always possible to expand  $\mathbf{G}(x)$  into two parts, first, the cosymmetry of  $\nabla_x \mathcal{V}(x)$ ,  $\nabla_x \mathcal{V}(x) \cdot \mathbf{G}_1(x) = 0$  for all  $x \in \mathcal{M}$ , and the other  $\nabla_x \mathcal{V}(x) \cdot \mathbf{G}_2(x)$  that is vanishing on average only.

#### *$\vartheta$ -expressions form a linear system*

Consider a set of  $\vartheta$ -expressions  $\Theta_1, \Theta_2, \Theta_3, \dots$ . Then the following properties are easily verified:

For any two  $\vartheta$ -expressions  $\Theta_1, \Theta_2$  their sum is  $\vartheta$ -expression, such that

- $\Theta_1 + \Theta_2 = \Theta_2 + \Theta_1$ ,
- $\Theta_1 + (\Theta_2 + \Theta_3) = (\Theta_1 + \Theta_2) + \Theta_3$ ,
- for all  $\vartheta$ -expressions,  $\Theta + 0 = \Theta$ ,
- for every  $\vartheta$ -expression  $\Theta + (-\Theta) = 0$ .

For an arbitrary  $\vartheta$ -expression  $\Theta$  and number  $a$  their product,  $a\Theta$ , is defined such that

- $a(b\Theta) = (ab)\Theta$  and  $1\Theta = \Theta$ .

The addition and multiplication operations are related as follows:

- $(a + b)\Theta = a\Theta + b\Theta$  and  $a(\Theta_1 + \Theta_2) = a\Theta_1 + a\Theta_2$ .

### Examples

It should be noted that only a few specific  $\vartheta$ -expressions have been used so far and described in the literature (*e.g.* [3, 4, 9, 11]), 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,  $\mathcal{V}(x) = H(x)$ ,  $\mathbf{G}(x) = \mathbf{J}\nabla H(x)$ ,  $H(x)$  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  $\vartheta$ -expressions are:

- The kinetic  $\vartheta$ -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  $\vartheta$ -expression,

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

The quantity  $\mathbb{V}(q) = \sum_{i=1}^N \mathbf{q}_i \cdot \nabla_{\mathbf{q}_i} V(q)$ , 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  $\vartheta$ -expression,

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

- Generalized  $\vartheta$ -expression,

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

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

Remark: The above examples are special cases of the latter, 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  $\vartheta$ -expressions is by direct calculation.

## 4. $\vartheta$ -expressions: an extended set

### Multi-index notation

In what follows we utilize the multi-index notation as described in [14].

Multi-index  $m$  is a set (vector)  $m = (m_1, m_2, \dots, m_n)$ , where  $m_i \in \mathbb{Z}_+$ , that is,  $\{m_i\}$  are non-negative integers. Let  $m$  be a multi-index, then

$$\begin{aligned} |m| &= m_1 + m_2 + \dots + m_n, \\ m! &= m_1! m_2! \dots m_n!, \\ \varphi^m(x) &= \varphi_1^{m_1}(x) \varphi_2^{m_2}(x) \dots \varphi_n^{m_n}(x), \end{aligned}$$

where  $\varphi(x) = (\varphi_1(x), \varphi_2(x), \dots, \varphi_n(x))$  is a vector field. Concerning multi-index derivatives we set

$$\begin{aligned} \partial &= (\partial_1, \partial_2, \dots, \partial_n) \equiv \left( \frac{\partial}{\partial x_1}, \frac{\partial}{\partial x_2}, \dots, \frac{\partial}{\partial x_n} \right), \\ \partial^m &= \partial_1^{m_1} \partial_2^{m_2}, \dots, \partial_n^{m_n}; \quad D^m = D_1^{m_1} D_2^{m_2}, \dots, D_n^{m_n}, \\ D_i &\equiv -\vartheta \partial_i; \quad D^m = (-\vartheta)^{|m|} \partial^m. \end{aligned}$$

#### 4.1. An extended set of $\vartheta$ -expressions

A  $\vartheta$ -expression is by definition a scalar function that satisfies the condition (2). Structurally, we define a set of  $\vartheta$ -expressions of the form,

$$\Theta_m(x, \theta) = \exp \{ \vartheta^{-1} \mathcal{V}(x) \} D^m \cdot [ \varphi^m(x, \vartheta) \exp \{ -\vartheta^{-1} \mathcal{V}(x) \} ], \quad (5)$$

where  $|m| \geq 1$ , dot denotes component-wise multiplication of vectors, and the vector field  $\varphi(x, \vartheta)$  satisfies some integrability conditions so that equation (2) is valid. Dependence of  $\varphi(x, \vartheta)$  on  $\vartheta$  is optional. However, it is allowed to use  $\varphi(x, \vartheta)$  as a vector of  $\vartheta$ -expressions. This fact is of particular importance in the context of improving the reliability of deterministic thermostat schemes.

First, we will prove that the above examples of  $\vartheta$ -expression are special cases of the expression (5). Since  $\vartheta$ -expressions are a linear system, let us consider the sum over all solutions of the Diophantine equation  $m_1 + m_2 + \dots + m_n = 1$ ,

$$\Theta^{(1)}(x, \theta) = \sum_{|m|=1} \Theta_m(x, \theta). \quad (6)$$

In virtue of the following easily verified equality,

$$\begin{aligned} \exp \{ \vartheta^{-1} \mathcal{V}(x) \} (-\vartheta \partial_i) (\varphi_i(x, \vartheta) \exp \{ -\vartheta^{-1} \mathcal{V}(x) \}) &= \varphi_i(x, \vartheta) \partial_i \mathcal{V}(x) - \vartheta \partial_i \varphi_i(x, \vartheta), \\ i &= 1, 2, \dots, n, \end{aligned}$$

we can rewrite the expression (6) as

$$\Theta^{(1)}(x, \vartheta) = \varphi(x, \vartheta) \cdot \nabla_x \mathcal{V}(x) - \vartheta \nabla_x \cdot \varphi(x, \vartheta), \quad (7)$$

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

Just for example, let the vector field  $\varphi(x, \vartheta)$  in the  $\vartheta$ -expression (7) be

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

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

$$\Theta^{(2)}(x, \vartheta) = \left( \psi(x, \vartheta) \circ \nabla_x \mathcal{V}(x) - \vartheta \nabla_x \circ \psi(x, \vartheta) \right) \cdot \nabla_x \mathcal{V}(x) \\ - \vartheta \nabla_x \cdot \left( \psi(x, \vartheta) \circ \nabla_x \mathcal{V}(x) - \vartheta \nabla_x \circ \psi(x, \vartheta) \right).$$

The described procedure can be repeated as needed. This type of mapping from  $\vartheta$ -expression to  $\vartheta$ -expression is definitely not unique. Depending on which physical system is to be studied at constant temperature, we have the freedom to determine in some sense the most appropriate  $\vartheta$ -expression and, therefore, the corresponding thermostat.

Regarding the general expression (5), we notice that  $\Theta_m(x, \theta)$  is a polynomial in  $\vartheta$  of degree  $|m|$ . The highest coefficient of this polynomial, that is, of  $\vartheta^{|m|}$ ,

$$\Theta_m(x, \theta) = (-1)^m (\partial^m \cdot \varphi^m(x)) \vartheta^{|m|} + \vartheta^{|m|-1}(\dots) + \dots,$$

where it is assumed that  $\varphi$  does not depend on  $\vartheta$ . Case  $|m| = 1$  is the most common in the literature, but higher order polynomials are also found, for example [12].

In our separate work [15], we pay attention to the specific case when  $\psi$  sequentially takes values,  $x$ ,  $(\circ x)^2$ ,  $(\circ x)^3$ , etc., and for comparison with thermostats often found in the literature, we perform test numerical simulations.

## 5. Conclusion

We have presented an extended set of temperature expressions with promising properties such that their application will be explored in our next work.

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