Notes on configurational thermostat schemes

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(Received 25 March 2010; accepted 24 May 2010; published online 30 June 2010)

[doi:10.1063/1.3453655]

I. INTRODUCTION

The simulation of rheological properties of molecular fluids requires realistic temperature control correctly taking into account the streaming velocity of the fluid. This has become feasible following the introduction of thermostatting techniques defining temperature using only configurational variables. Configurational approaches are also important in many other contexts, for example, in systems subject to an external pressure constraint and in understanding conformational dynamics of biomolecules.

In a series of papers,[1–4] Braga and Travis (BT) proposed a Nosé–Hoover type thermostat based on a configurational definition of temperature (in short BT thermostat), removing difficulties associated with the earlier Delhomelle–Evans approach,[5] which, for example, does not preserve the canonical distribution in the equilibrium case. Recently, the BT thermostat has had further attention, development, and application in the literature.[6–11] In the principal paper,[1] the authors considered the configurational thermostat scheme proposed in Refs. 12 and 13 (Samoletov-Dettmann-Chaplain, in short, SDC scheme) as a starting point and then presented their own configurational temperature thermostat as a further development of the SDC scheme. Correct action of both BT and SDC thermostats has been confirmed by a variety of numerical simulations in these works.

In this note, we link together two above-mentioned contributions in the development of configurational thermostats and thus accomplish two goals. First, we show that the configurational temperature BT thermostat is a particular case of the SDC scheme. Second, we demonstrate how this particular case benefits from the general method[12,13] in a variety of aspects including the physical context, a stochastic counterpart thermostat (to the authors' knowledge, this has not previously appeared in the literature), and ergodicity issues.

II. THE CONFIGURATIONAL TEMPERATURE THERMOSTAT

Let us clearly state in what way the BT thermostat is a particular case of the SDC scheme. The general SDC scheme[12,13] involves two different definitions of the configurational temperature and the corresponding double temperature control (for example, to allow control at two time scales), coupling between thermostats, anisotropy, and a series of definitions of the thermostat variable that does not directly relate to a particular temperature control. To reduce this general configurational thermostat method to the BT equations (our first goal), consider the simplified version of the SDC scheme where the virial temperature control and the coupling of thermostat variables are omitted,

$$m_k\dot{\mathbf{q}}_k = -\tau\nabla_{\mathbf{q}_k}V(\boldsymbol{q}) + \boldsymbol{\xi}_k,$$

$$\dot{\tau} = \frac{1}{Q_{\tau\tau}}\sum_{k=1}^{N}\frac{1}{m_k}[(\nabla_{\mathbf{q}_k}V)^2 - k_\mathrm{B}T\Delta_{\mathbf{q}_k}V].$$

Then consider the dynamic variables $\boldsymbol{\xi}_k$ according to the case (*a*) in Refs. 12 and 13 (variables $\boldsymbol{\xi}$ for all particles of the system are varied independently),

$$\dot{\boldsymbol{\xi}}_k = -\frac{1}{Q_{\xi\xi}}\frac{1}{m_k}\nabla_{\mathbf{q}_k}V(q),$$

set $Q_{\xi\xi}=1$, and finally define the canonical variables, $\mathbf{r}_k=\sqrt{m_k}\mathbf{q}_k$ and $\mathbf{p}_k=\sqrt{m_k}\boldsymbol{\xi}_k$. As a result, we arrive at the BT equations as a particular case of the more general SDC scheme,

$$\dot{\mathbf{r}}_k = \frac{\mathbf{p}_k}{m_k} - \tau\nabla_{\mathbf{r}_k}V, \quad \dot{\mathbf{p}}_k = -\nabla_{\mathbf{r}_k}V,$$
$$\dot{\tau} = \frac{1}{Q_{\tau\tau}}\sum_{k=1}^{N}[(\nabla_{\mathbf{r}_k}V)^2 - k_\mathrm{B}T\Delta_{\mathbf{r}_k}V]. \qquad (1)$$

It is easy to show that the canonical distribution, $\exp[-(1/k_\mathrm{B}T)(\Sigma(\mathbf{p}^2/2m)+V)]$, is invariant for this dynamics.

In the following paragraphs, we demonstrate in what way the SDC scheme contributes to the understanding of the configurational temperature thermostats.

A frequent problem, even if the canonical measure is invariant for the dynamics (1), is that only ergodic dynamics correctly samples the canonical distribution. In general, this condition is very difficult to prove for systems with many degrees of freedom. In particular, simple one-dimensional systems[14] reveal a difficulty and provide an important challenge for deterministic thermostatting methods. On the other hand, stochastic dynamics is typically ergodic.[15,16]

III. THE STOCHASTIC COUNTERPART

The Nosé–Hoover thermostat is a deterministic counterpart of the Langevin stochastic dynamics (e.g., Ref. 13). This fact is useful to determine the appropriate characteristic time scale of the dynamics. To clarify the physical sense of the configurational temperature thermostat, we formulate a stochastic counterpart of the dynamics (1). For the sake of brevity, we provide only the stochastic dynamics and its justification. A formal analysis can be done following the method presented in Refs. 17 and 18.

A particle of mass m in a dissipative medium under the influence of a constant force F has achieved the constant velocity $v_s = \tau F$, where τ is the mobility, after the transient time, $\sim m\tau$. We take into account the mobility as a perturbation of velocities. Explicitly, consider the following stochastic equations of motion:

$$\dot{\mathbf{q}}_k = \frac{\mathbf{p}_k}{m_k} - \tau \nabla_{\mathbf{q}_k} V(q) + \sqrt{2D}\mathbf{f}_k(t), \qquad \dot{\mathbf{p}}_k = - \nabla_{\mathbf{q}_k} V(q), \tag{2}$$

where $\{\mathbf{f}_k(t)\}$ is the set of independent standard "white noises." The Fokker–Planck equation corresponding to Eq. (2) has the form

$$\partial_t \rho = \sum_{(k)} \left\{ - \nabla_{\mathbf{q}_k} \left[\left(\frac{\mathbf{p}_k}{m_k} - \tau \nabla_{\mathbf{q}_k} V \right) \rho \right] + \nabla_{\mathbf{p}_k} \cdot (\nabla_{\mathbf{q}_k} V \rho) + D \Delta_{\mathbf{q}_k} \rho \right\} \equiv \mathcal{F}^* \rho, \tag{3}$$

where $\mathcal{F}^*$ is the Fokker–Planck operator. These stochastic dynamics can be generalized to the case of the state dependent mobility, $\tau \to \tau\varphi(p)$, where $\varphi(p)$ is a positive function of momenta. The Fokker–Planck equation $\partial_t \rho = \mathcal{F}^*_\varphi \rho$ corresponding to that case has the form (3), where $\tau \to \tau\varphi(p)$ and $D \to D\varphi(p)$. Indeed, suppose τ and D are connected to each other by the relation $D = \tau k_B T$. Substituting the canonical distribution, $\rho \sim \exp[-\beta(\Sigma_{(k)}(2m_k)^{-1}\mathbf{p}_k^2 + V(q))]$, into $\mathcal{F}^*_\varphi \rho$ and then applying the condition, $D = \tau k_B T$, we arrive at the identity, $\mathcal{F}^*_\varphi \rho \equiv 0$. Thus the canonical measure, $d\mu \sim \rho \Pi_{(k)} d\mathbf{q}_k d\mathbf{p}_k$, is invariant for this dynamics, and we obtain the stochastic counterpart of the deterministic configurational thermostat (1). The standard case is $\varphi(p) \equiv 1$ and $\mathcal{F}^* \rho \equiv 0$. The more general case, $\varphi = \varphi(p,q)$, can be considered, but in that case, we must specify the interpretation of the stochastic equations (Itô or Stratonovich) and correspondingly add an extra drift term into Eq. (2).

IV. THE EXTENDED CONFIGURATIONAL THERMOSTAT

Following the general SDC scheme,[12,13] the deterministic BT thermostat (1) can be refined in the following manner. Consider the extended dynamical system,

$$\dot{\mathbf{r}}_k = \frac{\mathbf{p}_k}{m_k} - \tau \nabla_{\mathbf{r}_k} V + \boldsymbol{\xi}_k, \quad \dot{\mathbf{p}}_k = - \nabla_{\mathbf{r}_k} V, \qquad \dot{\tau} = \frac{1}{Q_{\tau\tau}} \sum_{k=1}^{N} [(\nabla_{\mathbf{r}_k} V)^2 - k_B T \Delta_{\mathbf{r}_k} V], \quad \dot{\boldsymbol{\xi}}_k = \mathbf{h}_k, \tag{4}$$

where $\{\boldsymbol{\xi}_k\}$ are additional dynamical variables. Functions $\{\mathbf{h}_k\}$ can be fixed in a variety of forms as described in Refs. 12 and 13. For example, set $\mathbf{h}_k = -1/Q_\xi \Sigma_{(i)} \nabla_{\mathbf{r}_i} V$ for all particles of the system. Then the canonical measure (augmented with the Gaussian measure for thermostat variables τ and $\boldsymbol{\xi}$) is invariant for dynamics (4). In that case, the velocity of the center of inertia of a system dynamically fluctuates around zero with mobility Q_ξ^{-1}, where Q_ξ is a parameter.

V. ON ERGODICITY

The thermostat dynamics is able to correctly sample the canonical distribution only if the motion is ergodic. To improve ergodicity, we proposed in Ref. 13 to perturb the dynamics of the augmented thermostat variables (the Gaussian invariant measure for these variables is supposed) by additional random noise. This method was further investigated together with mathematical justification in Refs 15 and 16; Ref. 16 contains a formal generalization of the relevant thermostat schemes along with a general condition for checking the conservation of canonical ensemble. The numerical effectiveness of this method was also confirmed.[13,15,16] Taking into account additional advantages of this method including the "gentle" action of the stochastic term,[15,16] we propose to apply it to configurational temperature thermostats (1) and (4) similarly to the description in Ref. 13. For example, in set (1), we propose to perturb the dynamics of τ-variable by the white noise $f(t)$,

$$\dot{\tau} = \frac{1}{Q_{\tau\tau}} \sum_{k=1}^{N} [(\nabla_{\mathbf{r}_k} V)^2 - k_B T \Delta_{\mathbf{r}_k} V] - \Lambda\tau + \sqrt{2\mathrm{D}} f(t),$$

where (positive) Λ and D are connected to each other by the relation $k_B T \Lambda = \mathrm{D} Q_{\tau\tau}$. Then the augmented canonical measure is invariant for the dynamics. We conjecture that this is the unique invariant measure (compare with Ref. 15).

VI. CONCLUSION

In this Note, we have linked together two contributions in the development of configurational thermostats, the BT thermostat and the SDC scheme. We have shown that proposed configurational thermostats[1–4] are generalized and enriched in both understanding and content by the SDC scheme. We have presented the stochastic counterpart (2) to the configurational thermostat (1).

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