Constrained systems and statistical distribution

Simone Melchionna
Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1 EW, United Kingdom
(Received 3 May 1999; revised manuscript received 11 February 2000)

Theoretical advances in the statistical description of non-Hamiltonian systems [Tuckerman, Mundy, and Martyna, Europhys. Lett. **45**, 149 (1999)] have recently led us to rethink the definition of the phase-space probability by using the proper invariant measure. Starting from this point of view, we will derive the statistical distribution of constrained systems, considered as non-Hamiltonian, in Cartesian coordinates, in a way independent from the standard Lagrangian treatment. Furthermore, we will analyze the statistical distribution of the Nosé-Hoover isothermal (canonical or NVT) dynamics, considering with care the conservation laws hidden in the evolution equations. Consequently, we will correct the equations of motion in order to obtain the proper statistical ensemble. The isobaric-isothermal (constant pressure or NpT) form of the Nosé-Hoover dynamics is then considered as a nontrivial extension of the described procedure and, similarly to the NVT case, we will correct the equations of motion with respect to previous versions. The case of a constrained system coupled to a thermostat and a piston is easily handled by means of the same formalism, whereas the Lagrangian treatment becomes involved.

PACS number(s): 05.20.Gg, 05.70.Ce

I. INTRODUCTION

The statistical description of generic dynamical systems is the main task of statistical mechanics. Recently, Tuckerman *et al.* have analyzed the probability associated to non-Hamiltionian dynamics and have pointed out that a proper treatment of the problem is possible only by defining the invariant measure in phase space [1]. The authors have suggested viewing the phase-space in terms of a Riemannian manifold with a metric matrix whose determinant is determined by the evolution in time of the phase-space compressibility. The probability measure can then be written once the metric is known and all conservation laws exhibited by the dynamics have been detected.

In the present paper, we will consider the case of systems subjected to holonomic constraints viewed as generic non-Hamiltonian dynamics. For holonomic constraints, the equations of motion are either known from standard Lagrangian mechanics, if the unconstrained system is Lagrangian, or they can be written starting from Gauss's principle of least constraints in the more general case. The knowledge of the constrained probability is of importance for describing for example the behavior of semiflexible molecular systems in computer experiments. By applying the formalism of Tuckerman *et al.* we will derive the associated distribution function in Cartesian coodinates in a way alternative to the standard Lagrangian procedure [2].

Subsequently, we will apply the same theoretical analysis to study another interesting class of dynamics, the Nosé-Hoover (NH) thermostat and piston. The Nosé-Hoover scheme is a family of equations of motion customarily employed to achieve a phase-space trajectory sampling an isothermal [3,4] and/or isobaric ensemble [5,6]. By first considering the case of NH equations of motion without imposing any additional constraint, it can be shown [7,8] that the conservation of a pseudomomentum in [3–5] leads to an incorrect distribution function for both the NVT and NpT ensemble. In order to correct these distributions, we need to modify the NH equations so that the system conserves the physical momentum and the center-of-mass position (for internal forces summing to zero). The change corrects the previous NVT and NpT equations of motion [3–5] although the correction is numerically significant with respect to the previous version only for small systems with nonzero total momentum.

The more complex case of a constrained system coupled with the isobaric NH dynamics will be considered. This dynamical system leads to a heavy algebraic treatment if analyzed in terms of an underlying Lagrangian. Conversely, by applying the described procedure we will easily compute the probability measure, demostrating its simplicity.

The paper is organized as follows. In Sec. II the analytical treatment of constrained systems in terms of non-Hamiltonian systems is presented. Section III deals with the isothermal NVT dynamics with and without holonomic constraints. Section IV deals with the statistical distribution in the isobaric-isothermal ensemble with and without constraints. Section V contains some concluding remarks.

II. NON-HAMILTONIAN DYNAMICAL SYSTEMS AND HOLONOMIC CONSTRAINTS

Let us consider a generic non-Hamiltonian dynamical system composed of $x=\{x^i\}$ degrees of freedom and obeying the autonomous equations of motion

$$\dot{x}^i=\xi^i(x). \tag{1}$$

Tuckerman *et al.* [1] have recently shown that the invariant measure to be associated with the phase space of a non-Hamiltonian dynamics is not simply the Lebesgue measure, but it is the one obtained multiplying the volume element by $\sqrt{g(x)}$, where $g(x)$ is the determinant of the metric matrix of a general Riemann manifold. $g(x)$ is related to the Jacobian of the transformation of the phase-space point $x^0 \rightarrow x^t$,

 ©2000 The American Physical Society

$$\left\| \frac{\partial x^t}{\partial x^0} \right\| = \sqrt{g(x^0)}/\sqrt{g(x^t)}, \tag{2}$$

where $\sqrt{g(x)}$ satisfies the evolution equation [1]

$$\frac{d}{dt}\ln\sqrt{g(x)} = -\nabla\xi = -\sum_i \frac{\partial \xi}{\partial x^i} \tag{3}$$

showing that the metric is uniquely determined by the solution of the above differential equation, i.e., it is given in terms of the phase-space compressibility. The evolution for the metric is consistent with all conservation laws satisfied by the evolution equations. Writing the L conserved quantities as

$$\mathbf{C}(x) = \{C_\alpha(x)\}_{\alpha=1,L} = \mathbf{0}, \tag{4}$$

the ''microcanonical'' probability density will be given in the end by $\Pi_\alpha \delta(C_\alpha(x))$.

Following [1], we define the stationary distribution function $f(x)$ such that any ensemble average can be written as

$$\langle A \rangle = \frac{\int dx \sqrt{g(x)} f(x) A(x)}{\int dx \sqrt{g(x)} f(x)}, \tag{5}$$

where $\sqrt{g(x)} f(x) dx$ is the probability and $f(x)$ is the probability density [9].

Let us now consider a system described in Cartesian coordinates and subjected to holonomic constraints. In the following, we will use italic subscripts for atomic indexing, α and β for constraints, γ for molecular indices, and $\nu = 1,3$ for the spatial components of vectors. According to Hamiltonian dynamics of systems subjected to holonomic constraints, the equations of motion can be written in the form

$$\dot{r}_i = p_i/m_i,$$

$$\dot{p}_i = F_i + \sum_\alpha \lambda_\alpha \nabla_i \sigma_\alpha, \tag{6}$$

where the $\{\lambda\}$'s are the Lagrange multipliers whose values are obtained requiring that the G constraints

$$\sigma_\alpha(\{r\}) = 0,$$

$$\dot{\sigma}_\alpha(\{r,p\}) = \sum_i \nabla_i \sigma_\alpha \cdot p_i/m_i = 0, \quad \alpha = 1,G \tag{7}$$

are satisfied at any time. The above two conditions for σ and $\dot{\sigma}$ hold separately since they depend on positions and momenta as independent variables.

The set of equations (6), where the $\{\lambda\}$'s have been given their value $\lambda = \lambda(r,p)$, are not in Hamiltonian form but they have a simple form for the analytical treatment. Thus we regard the constrained evolution as a generic non-Hamiltonian dynamical system carrying a nontrivial metric. In the following we will consider the case of constraints that do preserve total momentum, such as constraints depending only on intramolecular distances.

The values of the Lagrange multipliers, which guarantee the constraints conservation, can be viewed as phase functions. In fact, by deriving twice in time the constraints, we obtain

$$\ddot{\sigma}_\alpha = \sum_{i,j} \nabla^2_{ij}\sigma_\alpha \frac{p_i \cdot p_j}{m_i m_j} + \sum_i \frac{\nabla_i \sigma_\alpha}{m_i} \cdot \left(F_i + \sum_\beta \nabla_i \sigma_\beta \lambda_\beta(r,p) \right) = 0 \tag{8}$$

so that

$$\lambda_\alpha(r,p) = -\sum_\beta Z^{-1}_{\alpha\beta} \left(\sum_{i,j} \nabla^2_{ij}\sigma_\beta \frac{p_i \cdot p_j}{m_i m_j} + \sum_i \frac{\nabla_i \sigma_\beta \cdot F_i}{m_i} \right), \tag{9}$$

where

$$Z_{\alpha\beta} = \sum_i \frac{\nabla_i \sigma_\alpha \cdot \nabla_i \sigma_\beta}{m_i} \tag{10}$$

is a symmetric matrix. Consequently, once we have substituted Eq. (9) in the equations of motion (6), the conditions $\sigma = \dot{\sigma} = 0$ no longer have to be added to the equations of motion but result as conservation laws produced by equations of motion of a non-Hamiltonian system.

The metric of the overall system can now be derived directly by computing the phase-space compressibility,

$$\begin{aligned} \frac{d\ln\sqrt{g}}{dt} &= -\sum_i \frac{\partial \dot{p}_i}{\partial p_i} = -\sum_{i,\alpha} \frac{\partial \lambda_\alpha}{\partial p_i} \nabla_i \sigma_\alpha \\ &= \sum_{i,j,\alpha,\beta} 2 Z^{-1}_{\alpha\beta} \nabla^2_{ij}\sigma_\beta \frac{p_i \cdot \nabla_i \sigma_\alpha}{m_i m_j} \\ &= \sum_{\alpha,\beta} Z^{-1}_{\alpha\beta} \dot{Z}_{\alpha\beta} = \mathrm{Tr}(Z^{-1}\dot{Z}) = \frac{d}{dt}\ln||Z|| \end{aligned} \tag{11}$$

(the last equality follows when considering the matrix U that diagonalizes Z, $Z = U^{-1}\tilde{Z}U$, and computing the trace $\mathrm{Tr}(Z^{-1}\dot{Z}) = \mathrm{Tr}[(U^{-1}\tilde{Z}^{-1}U)(-U^{-1}\dot{U}U^{-1}\tilde{Z}U + U^{-1}\dot{\tilde{Z}}U + U^{-1}\tilde{Z}\dot{U})] = \Sigma_\alpha(d\ln\tilde{Z}_{\alpha\alpha}/dt) = (d\ln||Z||/dt)$).

Hence, the constrained probability is simply obtained by considering all the conservation laws ($\sigma = \dot{\sigma} = 0, H = E$) and writing

$$f_\sigma \sqrt{g} d\Gamma = \delta(H-E) \prod_\alpha \delta(\sigma_\alpha)\delta(\dot{\sigma}_\alpha)||Z||d\Gamma, \tag{12}$$

where we have used the fact that the constraints do not make any work and therefore the energy is conserved. Thus by simply computing the phase-space compressibility, the metric of the constrained system and the total probability have been obtained, recovering the well known result of standard Lagrangian mechanics [2]. Furthermore, by using the concept of a Riemannian manifold for phase-space, the geometrical meaning of the invariant measure for a constrained

system has been uncovered, giving an intuitive picture of the effect of constraints in phase-space.

III. ISOTHERMAL NOSÉ-HOOVER DYNAMICS

The Nosé-Hoover dynamics is a nonlinear coupling between a Hamiltonian system and an additional degree of freedom introduced in order to thermalize the overall system [3,4]. This kind of thermalized dynamics is often used in order to attain a pseudocanonical sampling in computer simulations of molecular dynamics. The usual form of the NH equations of motion is

$$\begin{aligned} \dot{r}_i &= p_i/m_i, \\ \dot{p}_i &= F_i - \zeta p_i, \\ \dot{\zeta} &= \frac{2}{\tau_T^2 3NkT_o}(K - 3NkT_o/2), \\ \dot{s} &= 3Ns\zeta, \end{aligned} \tag{13}$$

where $K=\Sigma p_i^2/2m_i$, τ_T is a coupling time and T_o is the thermalization temperature, the latter being two free parameters. The NH equations have an irrelevant variable, s (Nosé variable), which is statistically independent from the set $\{r,p\},\zeta$. On the other hand the Nosé variable is useful to detect the conserved quantities, which are

$$\begin{aligned} H^c &= H + \tau_T^2 3NkT_o\zeta^2/2 + kT_o \ln s = \text{const}, \\ s^{1/3N}\mathbf{P}_o &= \text{const}, \end{aligned} \tag{14}$$

where H is the system Hamiltonian function and $\mathbf{P}_o=\Sigma\mathbf{p}_i$ is the system total momentum. The quantity $s^{1/3N}\mathbf{P}_o$ is conserved only if the sum of the system forces is strictly zero. Here those conserved quantities that are violated in practical cases, such as the angular momentum when using periodic boundary conditions, will not be considered.

The conservation laws show that the NH equations do not preserve total momentum, but only its product with the Nosé variable to the power $1/3N$. Therefore, the distribution associated with Eqs. (13) is not, strictly speaking, canonical, as already pointed out by Cho *et al.* [7] and Martyna [8], who have showed both numerically and analytically the effect of the bias produced by the conservation of $s^{1/3N}\mathbf{P}_o$ on the distribution for the Nosé equations of motion.

A modified version of the NH dynamics that conserves total momentum is

$$\begin{aligned} \dot{r}_i &= p_i/m_i, \\ \dot{p}_i &= F_i - \zeta(p_i - m_i P_o/M_o), \\ \dot{\zeta} &= \frac{2}{\tau_T^2 3NkT_o}\left(K - \frac{P_o^2}{2M_o} - \frac{3(N-1)kT_o}{2}\right), \\ \dot{s} &= (3N-3)s\zeta, \end{aligned} \tag{15}$$

where $M_o=\Sigma m_i$ is the total mass.

The equations conserve total momentum by construction (for zero total forces) and the conserved quantities are

$$\begin{aligned} H + \tau_T^2 3NkT_o\zeta^2/2 + kT_o \ln s &= \text{const}, \\ \mathbf{P}_o &= \text{const}. \end{aligned} \tag{16}$$

The system metric is flat in the $\{r,p\},\zeta,s$ variable set as it is for the original NH equations (although a metric factor is present if considering the $\{r,p\},\zeta$ set only) and the canonical distribution is obtained by integrating out the Nosé variable:

$$\begin{aligned} f^{NH}(r,p,\zeta) &= \int ds\, \delta(H^c - \text{const}) \prod_\nu \delta(P_{o\nu} - \text{const}) \\ &= \int ds\, \delta(H + \tau_T^2 3NkT_o\zeta^2/2 + kT_o \ln s \\ &\quad - \text{const}) \prod_\nu \delta(P_{o\nu} - \text{const}) \\ &\propto \exp[-\beta_o(H + \tau_T^2 3NkT_o\zeta^2/2)] \\ &\quad \times \prod_\nu \delta(P_{o\nu} - \text{const}). \end{aligned} \tag{17}$$

We can calculate the effect of coupling the Nosé variable to the absolute rather than to the relative momenta if the system is prepared at initial time with $\mathbf{P}_o(t=0)=0$ so that, given the evolution equation $\dot{\mathbf{P}}_o=-\zeta\mathbf{P}_o$, the condition $\mathbf{P}_o(t)=0$ will always hold. In this case the numerical trajectories with and without the correction differ by a factor $3kT_o/2$ in the kinetic balance in the evolution equation for $\dot{\zeta}$. Therefore, since the stationarity of the distribution in the two cases imposes that $\langle\dot{\zeta}\rangle=0$, we have $\langle K\rangle=3NkT_o/2$ for the original Nosé-Hoover dynamics and $\langle K\rangle=3(N-1)kT_o/2$ for the corrected one, the latter condition being compatible with the conservation of total momentum. The same result can be obtained by computing the probability directly for the original NH dynamics and by considering all the conservation laws, the result being $f\propto\exp[-\beta_o(N-1)/N(H+\tau_T^2 3NkT_o\zeta^2/2)]\delta(P_o)$. The difference in the trajectories is a shift in the average kinetic temperature, a bias that becomes negligible for large enough systems.

Let us now consider the Nosé-Hoover dynamics coupled to a constrained system. In this case the equations of motion are

$$\begin{aligned} \dot{r}_i &= p_i/m_i, \\ \dot{p}_i &= F_i + \sum_\alpha \tilde{\lambda}_\alpha \nabla_i \sigma_\alpha - \zeta(p_i - m_i P_o/M_o), \\ \dot{\zeta} &= \frac{2}{\tau_T^2(3N-G)kT_o}\left(K - \frac{P_o^2}{2M_o} - \frac{(3N-G-3)kT_o}{2}\right), \\ \dot{s} &= (3N-3-G)s\zeta. \end{aligned} \tag{18}$$

From the equations of motion it can be verified that the NH conserved quantity $H^c=H+\tau_T^2(3N-G)kT_o\zeta^2/2+kT_o\ln s$

is not violated by the constraints since $\Sigma_i \nabla_i \sigma_\alpha p_i/m_i = 0$, i.e., the conservation laws (16) are still both valid.

From the second time derivative of the constraints it follows that the Lagrange multipliers now depend on positions, momenta, and the thermostatting variable altogether,

$$\ddot{\sigma}_\alpha = \sum_{i,j} \nabla_{ij}^2 \sigma_\alpha \frac{p_i \cdot p_j}{m_i m_j} - \zeta \sum_i \frac{\nabla_i \sigma_\alpha \cdot p_i}{m_i} + \sum_i \frac{\nabla_i \sigma_\alpha}{m_i} \cdot \left(F_i + \sum_\beta \nabla_i \sigma_\beta \tilde{\lambda}_\beta(r,p,\zeta) \right) = 0, \quad (19)$$

where we have used the fact that for any vector v independent of the atomic indexes, the dependence of the constraints on the intramolecular distances only implies $\Sigma_i \nabla_i \sigma_\alpha \cdot v = 0$. Therefore,

$$\tilde{\lambda}_\alpha(r,p,\zeta) = \lambda_\alpha(r,p) + \zeta \sum_\beta Z_{\alpha\beta}^{-1} \sum_i \frac{\nabla_i \sigma_\beta \cdot p_i}{m_i}, \quad (20)$$

where λ_α and $Z_{\alpha\beta}$ are defined as in Eqs. (9) and (10). At this stage, the $\dot{\sigma}_\alpha = 0$ conditions are not yet imposed, i.e., the second term on the right-hand side of Eq. (20) is not set to zero, since this last term contributes to the compressibility. Proceeding analogously to the treatment for microcanonical constrained systems, the metric is

$$\frac{d \ln \sqrt{g}}{dt} = \mathrm{Tr}(Z^{-1}\dot{Z}) - \zeta \sum_{\alpha\beta} Z_{\alpha\beta}^{-1} Z_{\alpha\beta} + \zeta \sum_\nu \sum_i (1 - m_i/M_o) - (3N - 3 - G)\zeta = \frac{d \ln ||Z||}{dt} \quad (21)$$

and finally by again integrating out the Nosé variable we obtain

$$f_\sigma^{\mathrm{NH}}(r,p,\zeta)\sqrt{g}\, d\Gamma\, d\zeta \propto \exp\{-\beta_o[H + \tau_T^2 (3N-G) kT_o \zeta^2/2]\} \times ||Z|| \prod_\nu \delta(P_{o\nu} - \mathrm{const}) \times \prod_\alpha \delta(\sigma_\alpha)\, \delta(\dot{\sigma}_\alpha)\, d\Gamma\, d\zeta, \quad (22)$$

where we used the fact that the constraints conserve the Nosé-Hoover conserved quantity H^c.

IV. ISOTHERMAL-ISOBARIC NOSÉ-HOOVER DYNAMICS

The analysis of the distribution function in terms of the phase-space metric is useful for studying complex equations of motions, such as the ones for the isothermal-isobaric (NpT) case, where the algebraic treatment becomes involved.

The NpT dynamics has first been introduced by Andersen [10] and Nosé [3] and later written in the compact Nosé-Hoover form [5]. By first considering the case of an unconstrained system, we write the equations of motions of a system subjected to an external pressure A_o as

$$\dot{r}_i = p_i/m_i + \eta(r_i - R_o),$$

$$\dot{p}_i = F_i - (\zeta + \eta)(p_i - m_i P_o/M_o),$$

$$\dot{\zeta} = \frac{2}{\tau_T^2 3NkT_o}\left(K - \frac{P_o^2}{2M_o} - \frac{3(N-1)kT_o}{2} \right),$$

$$\dot{s} = (3N-3)s\zeta,$$

$$\dot{\eta} = \frac{V}{\tau_P^2 NkT_o}\left(\frac{2K + W - P_o^2/M_o}{3V} - A_o \right),$$

$$\dot{V} = 3V\eta, \quad (23)$$

where τ_P is the piston coupling time, K is the kinetic energy, and W is the atomic virial, and where we have corrected both the thermostat and the piston couplings with respect to the previous version in order to conserve total momentum. The conserved quantities are thus

$$H^c = H + \tau_T^2 3NkT_o \zeta^2/2 + kT_o \ln s + \tau_P^2 3NkT_o \eta^2/2 + A_o V = \mathrm{const},$$

$$\mathbf{P}_o = \mathrm{const}, \quad (24)$$

where again we only consider the case when total forces sum to zero. By computing the phase-space compressibility, we obtain

$$\frac{d \ln \sqrt{g}}{dt} = -3\eta = -\frac{d \ln V}{dt} \quad (25)$$

and therefore $\sqrt{g} \propto V^{-1}$. Setting the total momentum to zero, we include the constraint on the center-of-mass position $\mathbf{R}_o = \mathrm{const}$, since $\dot{\mathbf{R}}_o = \mathbf{P}_o/M_o$, so that the total probability is

$$f^{\mathrm{NH}}(r,p,\zeta,\eta,V)\sqrt{g}\, d\Gamma\, d\zeta\, d\eta\, dV \propto \int ds\, \delta(H^c - \mathrm{const}) \prod_\nu \delta(P_{o\nu})\, \delta(R_{o\nu} - \mathrm{const}) \times V^{-1} d\Gamma\, d\zeta\, d\eta\, dV \propto \exp[-\beta_o(H + \tau_T^2 3NkT_o \zeta^2/2 + \tau_P^2 3NkT_o \eta^2/2 + A_o V)] \prod_\nu \delta(P_{o\nu})\, \delta(R_{o\nu} - \mathrm{const})\, V^{-1} d\Gamma\, d\zeta\, d\eta\, dV. \quad (26)$$

The apparently odd V^{-1} term is indeed needed due to the conservation of the center-of-mass position. In fact, for the case of a perfect gas in the NpT ensemble and with conserved center-of-mass position, the partition function is proportional to

$$\int dV \exp(-\beta_o A_o V) \int d^N r \prod_\nu \delta(R_{o\nu} - \mathrm{const}) \propto \int dV \exp(-\beta_o A_o V) V^{N-1}. \quad (27)$$

Therefore, our distribution function correctly contains both the V^{-1} and the conservation of the center-of-mass position. The same argument applies for the nonideal case and for translational invariance of the potential, by writing the configurational integral in terms of scaled positions.

The equations of motion (23) differ from the previous NpT ones [5] by the coupling of the thermostat and piston to the relative rather than the absolute momenta. We rewrite here the latter for reference,

$$\begin{aligned}
\dot{r}_i &= p_i/m_i + \eta(r_i - R_o),\\
\dot{p}_i &= F_i - (\zeta+\eta)p_i,\\
\dot{\zeta} &= \frac{2}{\tau_T^2 3NkT_o}(K - 3NkT_o/2),\\
\dot{s} &= 3Ns\zeta,\\
\dot{\eta} &= \frac{V}{\tau_P^2 NkT_o}\left(\frac{2K_M + W_M}{3V} - A_o\right),\\
\dot{V} &= 3V\eta.
\end{aligned} \tag{28}$$

The effect of the coupling (28) is not dangerous for large systems. In fact, the metric corresponding to Eqs. (28) is $\sqrt{g}=1$, whereas the conserved quantities are the same extended enthalpy and the quantity $s^{1/3N}V^{1/3}\mathbf{P}_o$. The latter conserved quantity, which was not considered in previous treatments, introduces again a V^{-1} term in the distribution function. On the other hand, differently from Eqs. (23), the center-of-mass position is not conserved any more and therefore the resulting distribution function is incorrect.

As for the NVT case, the difference between the original and corrected equations of motion in this NpT case can be calculated once we set $\mathbf{P}_o = \mathbf{0}$ at initial time, thus ensuring its conservation at all times for the uncorrected equations of motion, since $\dot{\mathbf{P}}_o = -(\zeta+\eta)\mathbf{P}_o$. Again the stationarity of the distribution imposes $\langle\dot{\zeta}\rangle = \langle\dot{\eta}\rangle = 0$ and for the original equations $\langle K\rangle = 3NkT_o/2$, whereas for the corrected form $\langle K\rangle = 3(N-1)kT_o/2$. Therefore, the effect of coupling the thermostat and piston variables to the relative rather than the absolute momenta is negligible for large systems, since the original NpT equations sample the isobaric-isothermal ensemble with a temperature shifted by a factor $N/(N-1)$ with respect to the preset value T_o.

When considering the case of a constrained system in the NpT ensemble, we can couple the piston to the system in two different ways. Here we consider the simplest approach that consists in taking a set of molecules and couple the piston to the center-of-mass position of each molecule. In this case the equations of motion are written as

$$\begin{aligned}
\dot{r}_{\gamma i} &= p_{\gamma i}/m_{\gamma i} + \eta(R_\gamma - R_o),\\
\dot{p}_{\gamma i} &= F_{\gamma i} + \sum_\alpha \tilde{\lambda}_\alpha \nabla_{\alpha i}\sigma_\alpha - \zeta(p_{\gamma i} - m_i P_o/M_o)\\
&\quad - \eta m_{\gamma i}(P_\gamma/M_\gamma - P_o/M_o),\\
\dot{\zeta} &= \frac{2}{\tau_T^2(3N-G)kT_o}\left(K - \frac{P_o^2}{2M_o} - \frac{3(N-1)kT_o}{2}\right),\\
\dot{s} &= (3N-3-G)s\zeta,\\
\dot{\eta} &= \frac{V}{\tau_P^2 NkT_o}\left(\frac{2K_M + W_M - P_o^2/M_o}{3V} - A_o\right),\\
\dot{V} &= 3V\eta,
\end{aligned} \tag{29}$$

where $R_\gamma, P_\gamma, M_\gamma$ are the molecular center-of-mass positions, momenta, and masses, respectively. K_M, W_M are the molecular kinetic and virial contributions to pressure defined in [5]. The associated conserved quantities are

$$\begin{aligned}
&H + \tau_T^2(3N-G)kT_o\zeta^2/2 + kT_o\ln s + \tau_P^2 3NkT_o\eta^2/2 + A_oV\\
&\quad = \text{const},\\
&\mathbf{P}_o = \text{const} = 0,\\
&\mathbf{R}_o = \text{const},
\end{aligned} \tag{30}$$

and again the piston does not act against the intramolecular constraints ($\dot{\sigma} = \Sigma\nabla\sigma\dot{r} = \Sigma\nabla\sigma p/m = 0$). By repeating the same algebraic argument as for the NVT case, it is found that the Lagrange multipliers are still expressed by Eq. (20), due to the translational invariance of the constraints so that the piston dependent terms sum to zero in the corrispondent of Eq. (19) for the molecular NPT case. Therefore, the constrained isobaric-isothermal probability is

$$\begin{aligned}
&f_\sigma^{\mathrm{NH}}(r,p,\zeta,\eta,V)\sqrt{g}\,d\Gamma\,d\zeta\,d\eta\,dV\\
&\quad \propto \exp\{-\beta_o[H + \tau_T^2(3N-G)kT_o\zeta^2/2\\
&\qquad + \tau_P^2 3NkT_o\eta^2/2 + A_oV]\}\prod_\nu \delta(P_{o\nu})\,\delta(R_{o\nu} - \text{const})\\
&\qquad \times \prod_\alpha \delta(\sigma_\alpha)\,\delta(\dot{\sigma}_\alpha)V^{-1}||Z||\,d\Gamma\,d\zeta\,d\eta\,dV,
\end{aligned} \tag{31}$$

which is the expected NpT distribution function for a constrained system where the center of-mass position and momentum are conserved.

V. CONCLUDING REMARKS

The statistical distribution of constrained systems has been derived by considering the constrained dynamics as a non-Hamiltonian dynamical system. By using the generalized form of the Liouville equation and the phase-space compressibility, we have bypassed the Lagrangian treatment and computed directly the measure and, in turn, the probability density as a product of δ functions for each conserved quantity.

The method has proven to be advantageous when analyzing complex dynamical systems, such as the ones described for the isothermal-isobaric Nosé-Hoover dynamics coupled to constraints. For these cases, by detecting the conservation laws hidden in the NVT and NpT dynamics and by comput-

ing the associated metric, we have corrected the previous equations of motion for systems with total forces summing to zero in order to obtain the proper statistical distribution. The change consists in coupling the NH thermostat and piston to the relative rather than the absolute momenta and we have shown that the effect of the modification on numerical trajectories manifests itself only for small systems.

We conclude by remarking that we have detected the conserved quantities in the Nosé-Hoover dynamics by direct inspection. Other hidden conserved quantities may still be present. This could explain why the distribution computed for a single harmonic oscillator coupled to a NH thermostat is canonical, differing from the one derived numerically [11]. On the other hand, experience has shown that a thermalized system composed of many degrees of freedom exhibits a truly canonical distribution, therefore suggesting that the possible bias induced by other hidden conserved quantities is not important for large enough systems.

ACKNOWLEDGMENTS

I would like to thank Mark Tuckerman for a critical reading of the manuscript and Giovanni Ciccotti for several patient discussions concerning the subtleties of constraints and for important suggestions regarding the exposition of the subject.

[1] M.E. Tuckerman, C.J. Mundy, and G.J. Martyna, Europhys. Lett. **45**, 149 (1999).
[2] J.P. Ryckaert and G. Ciccotti, J. Chem. Phys. **78**, 7368 (1983).
[3] S. Nosé, J. Chem. Phys. **81**, 511 (1984).
[4] W.G. Hoover, Phys. Rev. A **31**, 1695 (1985).
[5] S. Melchionna, G. Ciccotti, and B.L. Holian, Mol. Phys. **78**, 533 (1993).
[6] G.J. Martyna, M.E. Tuckerman, G.J. Tobias, and M.L. Klein, Mol. Phys. **87**, 1117 (1996).
[7] K. Cho, J.D. Joannopoulos, and L. Kleinman, Phys. Rev. E **47**, 3145 (1993).
[8] G.J. Martyna, Phys. Rev. E **50**, 3234 (1994).
[9] M.E. Tuckerman, C.J. Mundy, S. Balasubramanian, and M.L. Klein, J. Chem. Phys. **108**, 4353 (1998).
[10] H.C. Andersen, J. Chem. Phys. **72**, 2384 (1980).
[11] M.E.Tuckerman, in *Classical and Quantum Dynamics in Condensed Phase Simulations*, edited by B.J. Berne, G. Ciccotti, and D.F. Coker (World Scientific, Singapore, 1997).