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Introduction of Andersen's demon in the molecular dynamics of systems with constraints

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The method of constant pressure molecular dynamics (MD), developed by Andersen for monoatomic fluids is extended to the MD, in Cartesian coordinates, of molecular systems with constraints. Andersen's proof is easily generalized after decoupling internal degrees of freedom from the center-of-mass. Only these last degrees are directly affected by Andersen's transformation (demon). The Cartesian equations of motion of individual atoms are derived from a generalized Andersen's Lagrangian. The equations are quite similar to those of the usual MD simulation at constant volume apart from an additional term coupling the molecular center-of-mass and the volume of the sample. The volume appears now as a dynamical variable evolving from the imbalance between imposed external pressure and instantaneous values of the molecular stress tensor. Some numerical aspects are discussed and the technique is briefly illustrated for the case of rigid diatomic molecules.

I. INTRODUCTION

Various methods of computer simulation are now available for the study, within a classical mechanics approach, of condensed matter. They correspond in statistical mechanics to different ensembles according to the imposed thermodynamical and mechanical conditions.

Monte Carlo (MC) simulations in the NPT (isobaric–isothermal) ensemble have been exploited some years ago for simple liquids[2(a)] and their mixtures[2(b)]; recently, a regain of interest for simulations in NPH (isobaric–isoenthalpic) and NPT ensembles has followed the publication of Andersen's method of constant pressure molecular dynamics.[1]

As it has been beautifully illustrated by the recent work of Parrinello and Rahman on solid rubidium,[3] a slightly modified version of the constant pressure simulation technique seems a very promising tool for testing interatomic or intermolecular interaction in connection with the crystal structures and structural phase transitions. In fact, it seems reasonable to expect that, especially in solids, to allow greater density fluctuations in the small systems usually considered in simulations could lead to a faster relaxation of a given system toward its equilibrium state. On the contrary, usual constant volume simulations might well probe metastable states as a result of the too rigid boundary conditions.

In Andersen's method and in its subsequent applications,[3,4] only monoatomic systems have been considered. It is therefore natural to look for a generalization of the constant pressure simulations to molecular systems. If the molecules consist of a collection of atoms interacting through analytical potentials, both MC and MD methods apply equally well as a set of molecules can be viewed formally as an atomic system. However, the molecular model often consists of partially or totally rigid molecules. Then the methods need to be adapted

in order to deal with the constraint relations.

Two different kinds of representation can be used when considering constrained systems. In the generalized coordinates approach, it seems natural to apply Andersen's demon to the center-of-mass of the molecules. With this choice, the volume fluctuations do not affect directly the internal structure of the molecule. This idea has been suggested by Brown[5] but it still needs a statistical mechanics justification, which in fact is easily found as a byproduct of the present work.

For rigid or semi-rigid molecules, the atomic description in terms of the Cartesian coordinates has proved to be very useful.[6,7] We have to adapt both the MC and Andersen methods to this atomic picture when the molecular model contains geometrical constraints. For the MC (in whatever ensemble), no recipe has been given so far to make a random move in terms of non-independent variables. On the contrary, Andersen's method can be generalized to yield a constant pressure version of the constant volume method of constraints.[6,7]

The object of the present paper is to present this dynamical representation of the isobaric–isoenthalpic ensemble for constrained systems represented by atomic Cartesian coordinates.

II. NVE AND NPH ENSEMBLES FOR MOLECULES WITH CONSTRAINTS

The Hamiltonian function H_1 associated to any molecular system can be written in terms of the Cartesian components of atomic positions $\{r_{i\alpha}\}$ and momenta $\{p_{i\alpha}\}$ (i and α indices denoting, respectively, specific atoms and molecules) as

$$H_1 = \sum_{1}^{N}{}_\alpha \sum_{1}^{n}{}_i \frac{\mathbf{p}_{i\alpha}^2}{2m_i} + V(\{r_{i\alpha}\}_{\substack{i=1,n \\ \alpha=1,N}}) , \qquad (1)$$

where V is the potential energy term which contains in general both inter and intramolecular contributions; N is the number of molecules, each of them being composed of n atoms.

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We are interested, in rigid (or partly rigid) molecules where constraint relations are imposed between atomic positions and momenta. Such relations are essentially of two kinds[7]:

(i) rigid bond constraints, where two atoms $i_{i\alpha}$ and $j_{j\alpha}$ are connected by a bond of fixed length d_{ij}; this implies that, at any time

$$(\mathbf{r}_{i\alpha} - \mathbf{r}_{j\alpha})^2 - d_{ij}^2 = 0 \ , \qquad (2)$$

(ii) linear vectorial constraints, where the position of a given atom $\mathbf{r}_{i\alpha}$ follows at any time from the coordinates of a set of n_b basic atoms $\{r_{\nu\alpha}\}$ through a linear relation with constant coefficients C_ν, i.e., $\nu = 1, n_b$,

$$\mathbf{r}_{i\alpha} - \sum_1^{n_b} {}_\nu C_\nu \mathbf{r}_{\nu\alpha} = 0 \ . \qquad (3)$$

(A simple example of this last constraints relation is provided by the rigid linear triatomic molecule where the coordinate of any atom can be written as a linear combination of the two other atomic positions.)

In classical mechanics, the constraint dynamics in Cartesian coordinates is most naturally obtained via the Lagrangian formalism[8]; standard MD simulations (at fixed NVE) have been implemented according to this atomic description.[6,7] The connection with statistical mechanics is the ergodic theorem which states that, given an arbitrary function $F(\{\mathbf{r}_{i\alpha}\}, \{\mathbf{p}_{i\alpha}\})$, $\bar{F}$, the time average of F over the (constrained) trajectory is equal to a corresponding microcanonical average F_{NVE}. In this last ensemble average, we need to restrict the phase space according to the constraints connecting the variables. However, together with the constraints relations (2) and (3), we have also to include the constraints on the atomic momenta which follow from the time derivatives of relations (2) and (3), i.e.,

$$(\mathbf{r}_{i\alpha} - \mathbf{r}_{j\alpha})(\mathbf{p}_{i\alpha}/m_i - \mathbf{p}_{j\alpha}/m_j) = 0 \ , \qquad (4)$$

$$\mathbf{p}_{i\alpha}/m_i - \sum_1^{n_b} {}_\nu C_\nu \mathbf{p}_{\nu\alpha}/m_\nu = 0 \ . \qquad (5)$$

The vectorial constraints (3) or (5) represent three scalar constraints. In order to simplify the notation, for a molecule subject to l scalar constraints, the whole family of constraints (2) and (3) and (4) and (5) can be written in a unified way, respectively, as

$$C_k^\alpha \equiv C_k^\alpha(\{\mathbf{r}_{i\alpha}\}) = 0 \ , \quad k = 1, l \ , \qquad (6)$$

$$\dot{C}_k^\alpha \equiv \dot{C}_k^\alpha(\{\mathbf{r}_{i\alpha}, \mathbf{p}_{i\alpha}\}) = 0 \ , \quad k = 1, l \ , \qquad (7)$$

where α denotes the molecule and k the constraint label. The microcanonical average F_{NVE} for a system of N identical molecules of n atoms subjected to l scalar constraints can be written in terms of Cartesian coordinates and momenta (see Appendix) as

$$F_{\mathrm{NVE}}(N, V, E) = [N! \Omega(N, V, E)]^{-1}$$
$$\times \int_V dr_{i\alpha}^{nN} \int d\mathbf{p}_{i\alpha}^{nN} \delta(H_1 - E)\delta_c F \ , \qquad (8)$$

where

$$\Omega(N, V, E) = (N!)^{-1} \int_V dr_{i\alpha}^{nN} \int d\mathbf{p}_{i\alpha}^{nN} \delta(H_1 - E)\delta_c \ , \qquad (8a)$$

$$\delta_c = \delta_c(\{\mathbf{r}_{i\alpha}, \mathbf{p}_{i\alpha}\})$$
$$= \prod_1^N {}_\alpha \prod_1^l {}_k \delta(C_k^\alpha)\delta\left(\sum_1^l {}_j Z_{\alpha,kj}^{-1} \dot{C}_j^\alpha\right) \ . \qquad (8b)$$

In Eq. (8b), $Z_{\alpha,kj}$ is the 1×1 matrix given by

$$Z_{\alpha,kj} = \sum_1^n {}_i \frac{1}{m_i} \frac{\partial C_k^\alpha}{\partial \mathbf{r}_{i\alpha}} \cdot \frac{\partial C_j^\alpha}{\partial \mathbf{r}_{i\alpha}} \ . \qquad (8c)$$

In Eq. (8), we adopt Andersen's notation for ensemble averages, here F_{NVE}(NVE), in which the subscript denotes the nature of the ensemble while the arguments represent numerical values of the ensemble parameters.

At this point, it is easy to introduce ensemble averages for the same mechanical system as defined by Eqs. (1)–(3). More specifically, we are presently interested to the NPH ensemble, the isobaric–isoenthalpic ensemble, for which we have

$$F_{\mathrm{NPH}}(N, P, H) = [N! \Gamma(N, P, H)]^{-1} \int_0^\infty dV \int_V dr_{i\alpha}^{nN}$$
$$\times \int d\mathbf{p}_{i\alpha}^{nN} \delta(H_1 + PV - H)\delta_c F \ , \qquad (9)$$

where

$$\Gamma(N, P, H) = (N!)^{-1} \int_0^\infty dV \int_V dr_{i\alpha}^{nN}$$
$$\times \int d\mathbf{p}_{i\alpha}^{nN} \delta(H_1 + PV - H)\delta_c \ . \qquad (9a)$$

The aim of this paper is to show how such ensemble averages F_{NPH} can be computed as time averages of $F(\mathbf{r}_{i\alpha}, \mathbf{p}_{i\alpha})$ over a phase space trajectory produced by a molecular dynamics simulation relative to a closely related but different mechanical system, first proposed by Andersen in the case of atomic fluids. In this new molecular system, a dynamical variable Q representing the volume of the sample will be coupled to the molecular center-of-mass without directly affecting the intramolecular structure of the molecules. This procedure will be developed in detail and justified in the next section; however, we will anticipate somewhat and rewrite F_{NPH} in terms of variables which precisely decouple the center-of-mass coordinates from intramolecular coordinates.

Let us define the molecular center-of-mass $\{\mathbf{R}_\alpha\}$, their associated total momenta $\{\mathbf{P}_\alpha\}$, and a suitable set of $6nN$ internal variables $\{\mathbf{s}_{i\alpha}, \mathbf{p}_{i\alpha}^s\}$ through the following transformation:

$$\mathbf{D}_\alpha \equiv \mathbf{R}_\alpha - (1/M)\sum_i m_i \mathbf{r}_{i\alpha} = 0 \ , \qquad (10)$$

$$\dot{\mathbf{D}}_\alpha \equiv (1/M)\left(\mathbf{P}_\alpha - \sum_i \mathbf{p}_{i\alpha}\right) = 0 \ , \qquad (11)$$

$$\mathbf{s}_{i\alpha} = \mathbf{r}_{i\alpha} - \mathbf{R}_\alpha \ , \qquad (12)$$

$$\mathbf{p}_{i\alpha}^s = \mathbf{p}_{i\alpha} - (m_i/M)\mathbf{P}_\alpha \ , \qquad (13)$$

where $M = \sum_i m_i$ is the total mass of the molecule. $\mathbf{D}_\alpha$ and $\dot{\mathbf{D}}_\alpha$ are symbols for the corresponding expressions.

Taking the defining relations (10) and (11) as linear vectorial constraints, the set of $6N(n+1)$ variables just defined gives an equivalent representation for the dy-

namical system given by the $6nN$ variables $\{\mathbf{r}_{i\alpha}, \mathbf{p}_{i\alpha}\}$ plus the Hamiltonian (1) and the constraints relations (6) and (7).

When performing this transformation, we find that:

(i) The Hamiltonian H_1 becomes

$$H_1 = \sum_1^N \left(\mathbf{P}_\alpha^2/2M + \sum_1^n (\mathbf{p}_{i\alpha}^s)^2/2m_i \right) + V(\{\mathbf{s}_{i\alpha} + \mathbf{R}_\alpha\}) . \quad (14)$$

(ii) It is easy to verify that the constraints relations (6), (7), and the matrix Z_α in Eq. (8c) are all independent from $\mathbf{R}_\alpha$, $\mathbf{P}_\alpha$, and maintain the same form with $\mathbf{s}(\mathbf{p}^s)$ replacing $\mathbf{r}(\mathbf{p})$

$$C_k^\alpha \equiv C_k^\alpha(\{\mathbf{s}_{i\alpha}\}) = 0 , \quad (6a)$$

$$\dot{C}_k^\alpha \equiv \dot{C}_k^\alpha(\{\mathbf{s}_{i\alpha}, \mathbf{p}_{i\alpha}^s\}) = 0 , \quad (7a)$$

$$\delta_c \equiv \delta_c(\{\mathbf{s}_{i\alpha}, \mathbf{p}_{i\alpha}^s\})$$
$$= \prod_1^N{}_\alpha \prod_1^l{}_k \delta(C_k^\alpha) \delta\left(\sum_1^l{}_j Z_{\alpha,kj}^{-1}(\{\mathbf{s}_{i\alpha}\}) \dot{C}_j^\alpha \right) . \quad (8d)$$

(iii) Relations (10) and (11) read

$$\mathbf{D}_\alpha \equiv (-1/M) \sum_i m_i \mathbf{s}_{i\alpha} = 0 , \quad (10a)$$

$$\dot{\mathbf{D}}_\alpha \equiv (-1/M) \sum_i \mathbf{p}_{i\alpha}^s = 0 . \quad (11a)$$

(iv) Any ensemble average can be written in terms of this new set of variables. For example, for the NPH ensemble one finds:

$$F_{\mathrm{NPH}}(N, P, H) = [N! \, \Gamma(N, P, H)]^{-1} \int_0^\infty dV \int_V d\mathbf{R}_\alpha^N \int d\mathbf{P}_\alpha^N \int d\mathbf{s}_{i\alpha}^{nN} \int d(\mathbf{p}_{i\alpha}^s)^{nN}$$
$$\times \delta(H_1 + PV - H) \delta_c \, \delta_{\mathrm{c.m.}} F(\{\mathbf{R}_\alpha + \mathbf{s}_{i\alpha}, \mathbf{p}_{i\alpha}^s + (m_i/M)\mathbf{P}_\alpha\}) , \quad (15)$$

where

$$\delta_{\mathrm{c.m.}} = \prod_\alpha \delta(\mathbf{D}_\alpha) \delta[(1/M)\dot{\mathbf{D}}_\alpha] . \quad (16)$$

The set $\{\mathbf{R}_\alpha, \mathbf{P}_\alpha, \mathbf{s}_{i\alpha}, \mathbf{p}_{i\alpha}^s\}$ will prove particularly useful to devise a dynamical evolution such that, for any property, a time average over this trajectory is equivalent to a NPH ensemble average.

III. GENERALIZATION OF ANDERSEN'S METHOD TO MOLECULES WITH CONSTRAINTS

As in Andersen's original paper,[1] our starting point is the Lagrangian function $\mathcal{L}_1$ for the system of interest, i. e., a system of N identical molecules of n atoms with l constraints, already considered in the previous section. In terms of the variables $\{\{\mathbf{s}_{i\alpha}\}_{i=1,n}, \mathbf{R}_\alpha\}_{\alpha=1,N}$ introduced in Eqs. (10) and (12), the Lagrangian can be written

$$\mathcal{L}_1 = \frac{1}{2} \sum_\alpha \left(\sum_i m_i \dot{\mathbf{s}}_{i\alpha} + M \dot{\mathbf{R}}_\alpha^2 \right) - V(\{\mathbf{s}_{i\alpha} + \mathbf{R}_\alpha\}) \quad (17)$$

with the associated constraint relations (6a) and (10a).

We now parallel Andersen procedure by introducing the Lagrangian

$$\mathcal{L}_2 = \frac{1}{2} \sum_\alpha \left(\sum_i m_i \dot{\sigma}_{i\alpha}^2 + MQ^{2/3} \dot{\rho}_\alpha^2 \right)$$
$$- V(\{\sigma_{i\alpha} + Q^{1/3} \rho_\alpha\}) + \frac{1}{2} M_p \dot{Q}^2 - P_{\mathrm{ext}} Q , \quad (18)$$

which is function of variables $\{\sigma_{i\alpha}, \rho_\alpha, Q\}$ to which, substituting $\sigma_{i\alpha}$ for $\mathbf{s}_{i\alpha}$, the constraint relations of the previous model are added. The Andersen transformation affects directly only the center-of-mass variables while adding the new variable Q. The range of variable ρ_α is now a cube of unit side, Q being an unrestricted positive variable. M_p is the inertial factor of the new variable Q and P_{ext} is a free parameter which will play in the following the role of the external pressure. This Lagrangian will generate the dynamics in which we are

interested.

The isobaric–isoenthalpic average of any observable F of the dynamical system defined by Eq. (17) can be explicitly evaluated as a time average of the corresponding observable over the dynamical trajectory defined by the Lagrangian (18). To formulate properly this statistical mechanics equivalence, we need the Hamiltonian formalism. The momenta $\{\pi_{i\alpha}, \pi_\alpha, \pi\}$ conjugate to the variables $\{\sigma_{i\alpha}, \rho_\alpha, Q\}$ are given by

$$\pi_{i\alpha} = \frac{\partial \mathcal{L}_2}{\partial \dot{\sigma}_{i\alpha}} = m_i \dot{\sigma}_{i\alpha} ,$$

$$\pi_\alpha = \frac{\partial \mathcal{L}_2}{\partial \dot{\rho}_\alpha} = MQ^{2/3} \dot{\rho}_\alpha , \quad (19)$$

$$\pi = \frac{\partial \mathcal{L}_2}{\partial \dot{Q}} = M_p \dot{Q}$$

in terms of which the Hamiltonian H_2 is

$$H_2 = \frac{1}{2} \sum_\alpha \left(\sum_i \pi_{i\alpha}^2/m_i + \pi_\alpha^2/MQ^{2/3} \right)$$
$$+ V(\{\sigma_{i\alpha} + Q^{1/3} \rho_\alpha\}) + \frac{1}{2} \pi^2/M_p + P_{\mathrm{ext}} Q . \quad (20)$$

We now define a correspondence between the variables of the new system and those of the original one, i. e.,

$$\mathbf{s}_{i\alpha} = \sigma_{i\alpha} , \qquad \mathbf{p}_{i\alpha}^s = \pi_{i\alpha} ,$$

$$\mathbf{R}_\alpha = Q^{1/3} \rho_\alpha , \qquad \mathbf{P}_\alpha = \pi_\alpha/Q^{1/3} , \qquad V = Q . \quad (21)$$

Using this correspondence, any observable of the original system $F(\{\mathbf{r}_{i\alpha}, \mathbf{p}_{i\alpha}\}, V) = F(\{\mathbf{s}_{i\alpha} + \mathbf{R}_\alpha, \mathbf{p}_{i\alpha}^s + (m_i/M)\mathbf{P}_\alpha\}, V)$ identifies an observable

$$\hat{F} \equiv F[\{\mathbf{r}_{i\alpha}(\sigma_{i\alpha}, \rho_\alpha, Q), \mathbf{p}_{i\alpha}(\pi_{i\alpha}, \pi_\alpha, Q)\}, Q] \quad (22)$$

for the new system. We can now closely follow Andersen demonstration.[1]

Using the ergodic theorem, we have as in Eq. (15):

$$\bar{F} = \hat{F}_{NVE}(N, 1, H)$$

$$= [N!\Omega_2(N, 1, H)]^{-1} \int d\pi \int_0^\infty dQ \int_1 d\rho_\alpha \int d\pi_\alpha \int d\sigma_{i\alpha}^{nN} \int d\pi_{i\alpha}^{nN} \, \delta(H_2 - H)\delta_c \, \delta_{c.m.} \hat{F} , \qquad (23)$$

where [see Eq. (8b)] $\delta_c = \delta_c(\{\sigma_{i\alpha}, \pi_{i\alpha}\})$ and

$$\delta_{c.m.} = \Pi_\alpha \delta(\mathbf{D}_\alpha)\delta[(1/M)\dot{\mathbf{D}}_\alpha] .$$

Changing the variables of integration through Eq. (21), one obtains

$$\bar{F} = \frac{\int_{-\infty}^{+\infty} d\pi \int_0^\infty dV \int_V d\mathbf{R}_\alpha \int d\mathbf{P}_\alpha \int d\mathbf{s}_{i\alpha}^{nN} \int d\mathbf{p}_{i\alpha}^{nN} \, \delta(H_1 + P_{ext} V + \pi^2/2M_\rho - H)\delta_c \, \delta_{c.m.} F}{\int_{-\infty}^{+\infty} d\pi \int_0^\infty dV \int_V d\mathbf{R}_\alpha \int d\mathbf{P}_\alpha \int d\mathbf{s}_{i\alpha}^{nN} \int d\mathbf{p}_{i\alpha}^{s,nN} \, \delta(H_1 + P_{ext} V + \pi^2/2M_\rho - H)\delta_c \, \delta_{c.m.}}$$

$$= \frac{\int_{-\infty}^{+\infty} d\pi \Gamma(N, P_{ext}, H - \pi^2/2M_\rho)F_{NPH}(N, P_{ext}, H - \pi^2/2M_\rho)}{\int_{-\infty}^{+\infty} d\pi \Gamma(N, P_{ext}, H - \pi^2/2M_\rho)} , \qquad (24)$$

where in the last step use has been made of definitions (9) and (9a).

The final part of Andersen proof applies now without any change. Therefore, expanding $F_{NPH}(N, P_{ext}, H - \pi^2/M_\rho)$ in a power series of $\pi^2/2M_\rho$ up to second order, performing explicit integration on variable π and recombining the terms, one finds

$$\bar{F} = F_{NPH}(N, P_{ext}, H - \bar{\pi}^2/2M_\rho) + O(N^{-2}) , \qquad (25)$$

provided that F is an intensive quantity. Otherwise the correction term would be of order $O(N^{-1})$. As in the case of atomic fluids, the average $\bar{\pi}^2/2M_\rho$ is an intensive quantity because it is equal to $1/2\,kT$ where T is the temperature of the new system in the microcanonical ensemble at $V = 1$ and $E = H$.

IV. EQUATIONS OF MOTION AND MOLECULAR DYNAMICS IMPLEMENTATION

A. Equations of motion

The Lagrangian formulation (18) of the "scaled" mechanical system is described in terms of a volume dynamical variable Q, $3N$ scaled center-of-mass positions ρ_α, and $3nN$ intramolecular variables $\sigma_{i\alpha}$ subjected to constraints (6a) and (10a). As Q and ρ_α are not involved in these constraints relations, their Lagrangian equations of motion are obtained using the standard procedure

$$\ddot{Q} = (1/M_\rho)\left\{(1/3Q)\left(\sum_\alpha MQ^{2/3}\dot{\rho}_\alpha^2\right.\right.$$

$$\left.\left. + Q^{1/3}\sum_\alpha \rho_\alpha \cdot \mathbf{F}_\alpha\right) - P_{ext}\right\} , \qquad (26)$$

$$\ddot{\rho}_\alpha = -(2/3)Q^{-1}\dot{Q}\rho_\alpha + Q^{-1/3}\mathbf{F}_\alpha/M , \qquad (27)$$

where

$$\mathbf{F}_\alpha = \sum_i \mathbf{F}_{i\alpha} = -\sum_i (\partial V/\partial\sigma_{i\alpha}) .$$

For variables $\sigma_{i\alpha}$ we derive the Lagrangian equation of the first kind with explicit constraint forces[8]; we find

$$m_i\ddot{\sigma}_{i\alpha} = \mathbf{F}_{i\alpha} - m_i\mu_\alpha - \sum_1^l \lambda_{k\alpha}(\partial C_k^\alpha/\partial\sigma_{i\alpha}) , \qquad (28)$$

where $\{\mu_\alpha\}$ and $\{\lambda_{k\alpha}\}$ are Lagrangian multipliers associated to constraints $\mathbf{D}_\alpha$ (10a) and C_k^α (6a), respectively.

Time deriving $\mathbf{D}_\alpha$ [Eq. (10a)] twice and substituting Eq. (28) for $\ddot{\sigma}_{i\alpha}$ we get $\mu_\alpha = \mathbf{F}_\alpha/M$. Equation (28) takes the form

$$m_i\ddot{\sigma}_{i\alpha} = \mathbf{F}_{i\alpha} - (m_i/M)\mathbf{F}_\alpha - \sum_1^l \lambda_{k\alpha}(\partial C_k^\alpha/\partial\sigma_{i\alpha}) . \qquad (28a)$$

We can now easily come back to the atomic variables $\mathbf{r}_{i\alpha}$ which are most common in MD simulation with Cartesian coordinates. Using the correspondence (21) and then Eq. (12), Eqs. (26), (27), and (28a) can be rewritten

$$m_i\ddot{\mathbf{r}}_{i\alpha} = \mathbf{F}_{i\alpha} - \sum_k \lambda_{k\alpha}(\partial C_k^\alpha/\partial\mathbf{r}_{i\alpha})$$

$$+ (m_i/3MV)[\ddot{V} - (2/3)V^{-1}\dot{V}^2]\sum_i m_i\mathbf{r}_{i\alpha} , \qquad (29)$$

$$M_\rho\ddot{V} = (3V)^{-1}\sum_\alpha [M(\dot{\mathbf{R}}_\alpha - (3V)^{-1}\dot{V}\mathbf{R}_\alpha)^2 + \mathbf{R}_\alpha \cdot \mathbf{F}_\alpha] - P_{ext} , \qquad (30)$$

where $\dot{\mathbf{R}}_\alpha$ and $\mathbf{R}_\alpha$ are no longer extra variables but short symbols for their definition in terms of $\mathbf{r}_{i\alpha}$, $\dot{\mathbf{r}}_{i\alpha}$. Moreover, if the dynamics corresponding to the Lagrangian (18) is expressed in terms of the variables $\{\mathbf{r}_{i\alpha}\}$ [Eqs. (29) and (30)] one can need the generalized momenta corresponding to $\{\mathbf{r}_{i\alpha}\}$. Using Eqs. (18), (12), (13), and (21) one finds $\mathbf{p}_{i\alpha} = m_i(\dot{\mathbf{r}}_{i\alpha} - (1/3Q)\dot{Q}\mathbf{R}_\alpha)$. For example, the temperature is given by the usual relation $\langle\sum_i \mathbf{p}_{i\alpha}^2/2m_i\rangle = (f/2)kT$, where f is the number of degrees of freedom of the molecule. It is apparent from Eq. (30) that the change of the volume come out simply from the difference between the trace of the molecular stress tensor and the external pressure. Equation (29) can be further simplified by explicitly solving for the Lagrangian multipliers corresponding to linear constraint relations. This implies a reduction of the variables. The technique to achieve this reduction is discussed in details elsewhere.[7]

B. MD implementation

Apart from the additional Eq. (30) and the last term in their right-hand side, Eqs. (29) are the usual equations of motion in Cartesian coordinates of a molecular

system with constraints. Their numerical implementation using the Verlet integration algorithm has been discussed in Refs. 6 and 7. This algorithm has proved to be very efficient. However, it applies directly only when the acceleration is independent from velocities. This is not true for the present equations but with a slight modification of the algorithm the simplicity of this integration still is useful. In the standard procedure, knowing the positions of all particles at time t and $t-h$ (where h is the time step and t the running time), one computes the positions at time $t+h$ and then the velocities at time t. The trajectory is obtained with an error of $O(h^4)$ while the velocities are computed with an error of $O(h^2)$. In the present case, with the knowledge of an extra configuration at time $t-2h$, one can predict velocities at time t, with a precision of order $O(h^2)$, using the formula

$$\mathbf{v}(t) = \frac{3\mathbf{r}(t) - 4\mathbf{r}(t-h) + \mathbf{r}(t-2h)}{2h} + O(h^2) \, . \tag{31}$$

This prediction can be used to compute the acceleration. One recovers the standard procedure with the same precision. The reason is that the acceleration appears with a h^2 factor.

C. Illustration

MD experiments of molecular systems at constant pressure can be performed with slightly modified versions of existing standard MD programs. We tested the present technique on the fluid of rigid homonuclear diatomic molecules considered in Ref. 9. The potential energy between two molecules is a sum of four site–site shifted Lennard-Jones (LJ) interactions $[v^s(r) = v(r) - v(r^*)$ for $r \le r^*$ and $v^s(r) = 0$ for $r > r^*]$, where $v(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$ and $r^* = 2.7\sigma$ is the adopted cutoff distance.

We first performed a standard MD experiment at a density of $\rho = 0.41\sigma^{-3}$ and $kT = 1.209\epsilon$ which corresponds to a dense liquid at normal temperature.

We then simulated the same system by a constant pressure–constant enthalpy MD according to Eqs. (29) and (30). The external pressure P_{ext} was fixed to the average pressure P_{NVE}(NVE) obtained in the first experiment and the total enthalpy was adjusted to

$$H = E + P_{ext} V + (1/2)kT \, , \tag{32}$$

where E, V, and T are, respectively, the total energy, volume, and average temperature relative to the NVE simulation (see Table I). The last term of the right-hand side of Eq. (32) is added to take into account the kinetic energy associated with the extra degree of freedom, i.e., the volume.

In both experiments, we considered a system of 216 molecules and adopted the time step $h = 0.003\sigma(M/\epsilon)^{1/2}$ (where M is the total mass of the molecule). In the same units, the total time τ of integration was, respectively, $\tau = 4.6$ and $\tau = 8.7$ for NVE and NPH simulations. In the NPH MD experiment we fixed the inertial factor associated with the volume to $M_p = 3.3 \times 10^{-4} \, M\sigma^{-4}$ as a similar value proved to be adequate for monoatomic LJ fluids.[4]

TABLE I. Comparison of NVE and NPH simulations of a liquid of homonuclear diatomic molecules at a similar thermodynamical state $\rho = 0.41\sigma^{-3}$, $kT = 1.2\epsilon$. If F is a fixed quantity its value is affected by the symbol *, while if F is a fluctuating quantity, δF is the rms deviation of F. (n_f is the total number of degrees of freedom, $H_s = E + PV$ is the total enthalpy of the system of interest while H is the total enthalpy including the kinetic energy associated to V.)

F	F_{NVE}	δF_{NVE}	F_{NPH}	δF_{NPH}
N	216*		216*	
n_f	1077*		1078*	
E/ϵ	−1281.09*	0.05[a]	−1282.6	b
kT/ϵ	1.209	0.029	1.201	0.043
$P/\epsilon\sigma^{-3}$	1.508	0.216	1.508*	
V/σ^3	526.8*		527.9	3.7
H_s/ϵ	−486.7	113.8	−486.6	b
H/ϵ			−485.98*	0.05[a]

[a]These numbers should theoretically be zero and are indicated here only to give the magnitude of the fluctuations due to the use of the numerical integration scheme.
[b]Quantities not evaluated.

In Table I, we list some fixed or averaged quantities relative to these experiments. The results suggest that both experiments are representative of the same thermodynamical state. Note finally the similar and good degree of conservation of the conserved quantities, i.e., the total energy in the NVE case and total enthalpy in the NPH case. Therefore, the modified version of the Verlet algorithm, introduced in our constant pressure simulation, does not introduce any numerical problem.

V. CONCLUSIONS

The extension of the constant pressure MD technique to molecular systems with constraints has been made possible by applying Andersen's scaling transformation to the molecular center-of-mass. This transformation was performed on the Lagrangian of the system of polyatomic molecules after substitution of atomic coordinates $\mathbf{r}_{i\alpha}$ by $\mathbf{s}_{i\alpha} + \mathbf{R}_\alpha$ where $\mathbf{s}_{i\alpha}$ is the position of atom i of molecule α relative to the center of mass $\mathbf{R}_\alpha$. Three additional variables per molecule have been introduced, and as a consequence, three constraint relations relating the $\mathbf{s}_{i\alpha}$ (but not $\mathbf{R}_\alpha$) have been included to the description [see Eqs. (17) and (10a)].

In the third section, we switched from the Lagrangian formalism to the Hamiltonian one to prove that time average on the scaled system corresponds to isobaric–isoenthalpic averages on the original system.

The equations of motion corresponding to the modified Lagrangian subject to all constraints were derived and written in terms of the usual Cartesian atomic coordinates in Sec. IV.

While these equations have been given within the framework of molecules with constraints treated in terms of the Cartesian atomic coordinates, they have wider implications.

(i) For unconstrained polyatomic molecules, they provide an alternative to the original Andersen's method

where the volume couples directly to individual atoms.

(ii) Summing Eqs. (29) yields the corresponding equations of motion of the molecular center-of-mass in our constant pressure MD. In this way, Brown's suggestion[5] can be justified and therefore, the present method can also be performed in generalized coordinates if one simply adds to the center-of-mass equations, mentioned above, the equations of motion relative to the internal coordinates which are unaltered.

We are presently investigating the use of HPN techniques to test molecular interaction models on molecular crystal structures at nonzero temperature.

For such a purpose the generalized tensorial version of the HPN method due to Parrinello and Rahman is very useful. With the present technique it is easy to adapt this version to the case of constrained molecules.

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APPENDIX

Let us introduce a set $\{q_{j\alpha}, p^q_{j\alpha}\}_{j=1,f}$ of $f = 3n - l$ independent generalized coordinates and conjugate momenta describing the mechanical state of molecule α ($\alpha = 1, N$) containing n atoms subject to the l geometrical constraints of Eq. (6).

Let us call $F^c(q, p^q)$ the dynamical variable equivalent to $F(\{r, p\})$ in Eq. (8),

$$F^c(\{q, p^q\}) = F(\{r(q), p(q, p^q)\}) \ . \tag{A1}$$

We now show that the familiar expression of the microcanonical average

$$F^c_{\text{NVE}} = [N! \Omega(N, V, E)]^{-1}$$
$$\times \int dq \, dp^q \, F^c(q \, p^q) \delta[H_c(q \, p^q) - E] \ , \tag{A2}$$

where

$$\Omega(N, V, E) = [N!]^{-1} \int dq \, dp^q \, \delta[H_c(q \, p^q) - E] \ , \tag{A3}$$

$$H_c(q \, p^q) = \frac{1}{2} \sum_1^N \sum_j^f \sum_k^f \bar{A}^{-1}_{\alpha j k} p^q_{j\alpha} p^q_{k\alpha} + V_c(\{q\}) \ , \tag{A4}$$

and

$$\bar{A}_{\alpha j k} = \sum_1^n m_i \frac{\partial \mathbf{r}_{i\alpha}}{\partial q_{j\alpha}} \cdot \frac{\partial \mathbf{r}_{i\alpha}}{\partial q_{k\alpha}} \tag{A5}$$

is equivalent to our Eq. (8).

The system is described in Cartesian coordinates by the Lagrangian

$$\mathcal{L}(r \, \dot{r}) = \sum_{i,\alpha} \tfrac{1}{2} m_i \dot{\mathbf{r}}^2_{i\alpha} - V(\{r\}) \ , \tag{A6}$$

to which we add the constraints relations, Eqs. (6). The corresponding dynamics is given by the Lagrange equations of motion of first kind.[8] Adding to the fN generalized coordinates q_α, the set of $l \times N$ constraints relations C^α, Eqs. (6), as new coordinates which complete the set, we have[10,11]

$$\mathbf{r}_\alpha = \mathbf{r}_\alpha(\{q_\alpha, C^\alpha\}) \equiv \mathbf{r}_\alpha(\{u\}) \ , \tag{A7}$$

where $u = \{u_{\alpha s}\}$, $s = 1, 3n$, $\alpha = 1, N$ is a short symbol for $\{q, C\}$. The Lagrangian in the new variables is given, in matricial notation, by

$$\mathcal{L}'(u, \dot{u}) = \frac{1}{2} \sum_1^N \dot{u}^T_\alpha M_\alpha \dot{u}_\alpha - V'(\{u\}) \ , \tag{A8}$$

where u^T is the transpose of vector u and

$$M_\alpha = \begin{pmatrix} A_\alpha & B_\alpha \\ B^T_\alpha & \Gamma_\alpha \end{pmatrix} \tag{A9}$$

is the metric matrix whose elements are given by

$$(M_\alpha)_{\mu\nu} = \sum_1^{3n} m_i \frac{\partial \mathbf{r}_{i\alpha}}{\partial u_\mu} \cdot \frac{\partial \mathbf{r}_{i\alpha}}{\partial u_\nu} \ . \tag{A10}$$

The submatrices A_α, B_α, Γ_α have as dimensions, respectively $(f \times f)$, $(f \times l)$, $(l \times l)$.

The corresponding Hamiltonian is given by

$$H'(u, p^u) = \frac{1}{2} \sum_1^N p^{uT}_\alpha M^{-1}_\alpha p^u_\alpha + V'(u) \ , \tag{A11}$$

where

$$p^u_\alpha = \frac{\partial \mathcal{L}'}{\partial \dot{u}_\alpha} = M_\alpha \dot{u}_\alpha \tag{A12}$$

and

$$M^{-1}_\alpha \equiv \begin{pmatrix} \Delta_\alpha & E_\alpha \\ E^T_\alpha & Z_\alpha \end{pmatrix} = \left(\sum_1^{3n} \frac{1}{m_i} \frac{\partial u_{\alpha\mu}}{\partial \mathbf{r}_{i\alpha}} \cdot \frac{\partial u_{\alpha\nu}}{\partial \mathbf{r}_{i\alpha}} \right) . \tag{A13}$$

The Lagrangian of the system with constraints is recovered from $\mathcal{L}'$ by putting in Eq. (A8) $C^\alpha = \dot{C}^\alpha = 0$.

For the Hamiltonian description we have

$$\dot{C}^\alpha = E^T_\alpha p^q_\alpha + Z_\alpha p^c_\alpha \ . \tag{A14}$$

Therefore, $\dot{C}^\alpha = 0$ corresponds to $p^c_\alpha = -\bar{Z}^{-1}_\alpha \bar{E}^T_\alpha p^q_\alpha$, where $^-$ means the matrices are evaluated at $C^\alpha = 0$. A direct calculation shows that the Hamiltonian of the constrained system is obtained for $C^\alpha = 0$, $p^c_\alpha = -\bar{Z}^{-1}_\alpha \bar{E}^T_\alpha p^q_\alpha$,

$$H_c(q_\alpha, p^q_\alpha) = H'(q_\alpha, p^q_\alpha, C_\alpha = 0, p^c_\alpha = -Z^{-1}_\alpha E^T_\alpha p^q_\alpha) \ . \tag{A15}$$

The explicit inversion of Eq. (A12) gives Eq. (A14), where $E^T_\alpha = Z_\alpha B^T_\alpha A^{-1}_\alpha$ and $Z_\alpha = (\Gamma_\alpha - B^T_\alpha A^{-1}_\alpha B_\alpha)^{-1}$. Then we have

$$p^c_\alpha + B^T_\alpha A^{-1}_\alpha p^q_\alpha = Z^{-1}_\alpha \dot{C}_\alpha \ . \tag{A16}$$

Finally we can write

$$F^c_{\text{NVE}} = [N! \Omega(N, V, E)]^{-1} \int dq \, dp^q \, F^c(q \, p^q) \delta[H_c(q \, p^q) - E]$$

$$= [N! \Omega(N, V, E)]^{-1} \int du \, dp^u \, F'(u \, p^u) \delta[H'(u \, p^u) - E] \delta(C) \delta(p^c + B^T A^{-1} p^q)$$

$$= [N! \Omega(N, V, E)]^{-1} \int dr\, dp\, F(r\,p) \delta[H(r\,p) - E] \delta(C) \delta(Z^{-1} \dot{C}) \; . \tag{A17}$$

The last equality follows from the fact that the variable transformation $(u, p^u) \to (r, p)$ is a point transformation, therefore a canonical one. Moreover the Jacobian of a canonical transformation is ± 1 because the volume is a canonical invariant.[12]

One can easily be convinced that the matrix M_α does not depend on R_α. Writing

$$\mathbf{r}_{i\alpha} = \mathbf{R}_\alpha + \sum_j \frac{m_j}{M} (\mathbf{r}_{i\alpha} - \mathbf{r}_{j\alpha}) \tag{A18}$$

and expressing the $\mathbf{r}_{i\alpha}$ in terms of $l + (f - 3)$ internal coordinates and constraint coordinates one immediately verifies that M_α, Eq. (A10), does not depend on R_α.

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