

# Pressure coupling / barostats

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## Abstract

This is a brief overview in terms of the journal club about pressure coupling in molecular dynamics (MD). It is far from being complete, also some formulas might be erroneous. For more details have a look the references.

## 1 Pressure

In some cases, it is important to simulate a system at constant pressure. As it was already a common practice to do that in Monte Carlo simulations, also algorithms for MD were developed. The first thing to start of is an expression for the pressure of a simulated system.

The pressure tensor  $\mathbf{P}$  can be calculated using Clausius virial theorem as

$$\mathbf{P} = \frac{2}{V} (\mathbf{E}_{kin} - \Xi) \quad (1)$$

with the box volume  $V$ , the kinetic energy  $\mathbf{E}_{kin}$  and the inner virial tensor

$$\Xi = -\frac{1}{2} \sum_{i < j} \mathbf{r}_{ij} \cdot \mathbf{F}_{ij}. \quad (2)$$

See e.g. Ref [1]. The isotropic pressure is calculated from the trace of the pressure tensor

$$P = \text{Tr}(\mathbf{P}) / 3. \quad (3)$$

Details of the derivation are described in the appendix.

## 2 Isotropic coupling

Correcting the pressure in a simulation can be achieved through a change in the inner virial  $\Xi$  by scaling the inter particle distances. This is the common procedure in all barostats described below.

## 2.1 Berendsen barostat

In the Berendsen method[2], the system is weakly coupled to an external bath using the principle of least local perturbation. Similar to the temperature coupling, an extra term is added to the equations of motion that effects a pressure change

$$\left(\frac{dp}{dt}\right)_{bath} = \frac{p_0 - p}{\tau_p} \quad (4)$$

where  $\tau_p$  is the time constant for the coupling. A simple proportional coordinate scaling, concomitant with volume scaling, minimizes local disturbances. An extra term is added to the equations of motion:

$$\dot{\mathbf{x}} = \mathbf{v} + \alpha \mathbf{x}, \quad (5)$$

while the volume changes accordingly:

$$\dot{V} = 3\alpha V. \quad (6)$$

The pressure change is related to the isothermal compressibility  $\beta$

$$\frac{dP}{dt} = -\frac{1}{\beta V} \frac{dV}{dt} = -\frac{3\alpha}{\beta}. \quad (7)$$

With Eq. 4  $\alpha$  evaluates to

$$\alpha = -\frac{\beta(p_0 - p)}{3\tau_p}. \quad (8)$$

Thus the modified equation of motion is

$$\dot{\mathbf{x}} = \mathbf{v} - \frac{\beta(p_0 - p)}{3\tau_p} \mathbf{x} \quad (9)$$

and represents a proportional scaling of coordinates.

The compressibility, that may not be accurately known, occurs in the expression for the scaling, but from Eq. 9 one can easily see, that only that ratio  $\beta/\tau_p$  enters in the equations of motion.

## 2.2 Andersen barostat

The Andersen method[3] was developed to adjust the pressure in a simulation of interacting particles. In the following description, only systems of pairwise interacting particles are treated. The method was later first extended to anisotropic coupling by Parrinello et al[4] and later also to molecular systems by Nosé et al[5].

Andersen proposed to replace the coordinates  $\mathbf{r}_i$  by scaled coordinates  $\rho_i$  defined as

$$\rho_i = \mathbf{r}_i/V^{1/3} \quad (10)$$

Consider the new Lagrangian, in which a new variable  $Q$  appears:

$$\mathcal{L}(\rho^N, \dot{\rho}^N, Q, \dot{Q}) = \frac{1}{2}Q^{2/3} \sum_{i=1}^N m_i \dot{\rho}_i^2 - \sum_{i<j=1}^N U(Q^{1/3} \rho_{ij}) + \frac{1}{2}M\dot{Q}^2 - p_0 Q. \quad (11)$$

If we interpret  $Q$  as the volume  $V$ , the first two terms on the right are just the Lagrangian of the unscaled system. The third term is a kinetic energy for the motion of  $Q$ , and the fourth represent a potential energy associated with  $Q$ . Here  $p_0$  and  $M$  are constants. A physical interpretation of the additional terms would be: Assume the system is simulated in a container and can be compressed by a piston. Thus,  $Q$ , whose value is the volume  $V$ , is the coordinate of the piston.  $p_0 V$  is the potential derived from an external pressure  $p_0$  acting on the piston and  $M$  is the mass of the piston.

In the original paper by Andersen, now follows some math, where the Hamiltonian is derived, out of that the equations of motion for the scaled system and finally mapping back to the real variables. Here I skip all the details and just give the equations of motion

$$\frac{d\mathbf{r}_i}{dt} = \frac{\mathbf{p}_i}{m_i} + \frac{1}{3}\mathbf{r}_i \frac{d \ln V}{dt}, \quad (12)$$

$$\frac{d\mathbf{p}_i}{dt} = - \sum \hat{\mathbf{r}}_{ij} U'(r_{ij}) - \frac{1}{3}\mathbf{p}_i \frac{d \ln V}{dt}, \quad (13)$$

$$\frac{Md^2V}{dt^2} = p_0 + \left( \frac{2}{3} \sum \frac{\mathbf{p}_i^2}{2m_i} - \frac{1}{3} \sum \mathbf{r}_{ij} U'(r_{ij}) \right) / V. \quad (14)$$

Add note from andersen paper on how to choose M!!

### 3 Anisotropic coupling

#### 3.1 Anisotropic Berendsen pressure coupling

There is also an anisotropic version of the Berendsen barostat, but this will not be treated in this summary.

#### 3.2 Parrinello-Rahman barostat

When simulating crystal structures, it is not sufficient only to scale the volume. Parrinello and Rahman extended the method proposed by Andersen the let the simulation box also change it's shape.

Let's start with some notation: The cell can have an arbitrary shape, it's volume completely described by three vectors  $\mathbf{a}$ ,  $\mathbf{b}$ ,  $\mathbf{c}$ . The vectors can have different lengths and arbitrary mutual orientations. An alternative description is obtained by arranging the vectors as  $\{\mathbf{a}, \mathbf{b}, \mathbf{c}\}$  to form a  $3 \times 3$  matrix  $\mathbf{h}$  whose columns are the latter vectors. The volume is given by

$$V = \det \mathbf{h} = \mathbf{a} \cdot (\mathbf{b} \times \mathbf{c}). \quad (15)$$

The position  $\mathbf{r}_i$  of a particle can be written in terms of  $\mathbf{h}$  and a column vector  $\mathbf{s}_i$ , with components  $\xi_i$ ,  $\eta_i$  and  $\zeta_i$  as

$$\mathbf{r}_i = \mathbf{h}\mathbf{s}_i = \xi_i \mathbf{a} + \eta_i \mathbf{b} + \zeta_i \mathbf{c} \quad (16)$$

with  $0 \leq \xi_i, \eta_i, \zeta_i \leq 1$ . The square of the distance between particle  $i$  and  $j$  is given by

$$r_{ij}^2 = \mathbf{s}_{ij}^T \mathbf{G} \mathbf{s}_{ij} \quad (17)$$

where the metric tensor  $\mathbf{G}$  is

$$\mathbf{G} = \mathbf{h}^T \mathbf{h}. \quad (18)$$

Using the latter notation, the Lagrangian can be written as

$$\mathcal{L} = \frac{1}{2} \sum m_i \dot{\mathbf{s}}_i^T \mathbf{G} \dot{\mathbf{s}}_i - \sum \sum U(r_{ij}) + \frac{1}{2} M \text{Tr}(\dot{\mathbf{h}}^T \dot{\mathbf{h}}) - pV \quad (19)$$

Deriving the equations of motion is similar to the isotropic case from Andersen.

## 4 Appendix

### A Pressure and the Clausius virial theorem

Starting from the equations of motion for an N-particle system

$$m_i \ddot{\mathbf{r}}_i = \mathbf{F}_i \quad j = 1, 2..N \quad (20)$$

with particle coordinates  $\mathbf{r}_i$ ,  $m_i$  and force  $\mathbf{F}_i$  acting on particle  $i$ . Multiplication with  $\mathbf{r}_i$  and using the relation

$$\mathbf{r} \ddot{\mathbf{r}} = \frac{d}{dt} (\mathbf{r} \dot{\mathbf{r}}) - \dot{\mathbf{r}}^2, \quad (21)$$

leads to

$$\frac{d}{dt} (m_i \mathbf{r}_i \dot{\mathbf{r}}_i) - m_i \dot{\mathbf{r}}_i^2 = \mathbf{F}_i \mathbf{r}_i \quad (22)$$

Averaging over all particles and time, the first term due to the derivation in time becomes zero. The second term is the total energy

$$\sum \overline{m_i \mathbf{r}_i^2} = 2E_{kin}. \quad (23)$$

The last term  $\sum_{i=1}^N \mathbf{F}_i \mathbf{r}_i$  is called the virial. Finally, Eq. 22 leads to

$$-2E_{kin} = \sum \overline{\mathbf{F}_i \mathbf{r}_i}. \quad (24)$$

Now we have a more detailed look at the virial term. We assume that the particles are trapped in a box with volume  $V$  and exert a pressure  $p$  onto the walls. In other terms, that means, that a wall element exerts a force  $p df$  onto nearby particles and is directed inside the box. This part of the virial we call  $W_a$ . The part due to particle-particle we call "inner virial" denoted as  $\Xi$ .

In Fig. 1, the force  $p df$  acting on particles arising from a wall element  $df$  is depicted. The acts on all nearby particles and is directed into the box. Since  $df$  is small, the positions  $\mathbf{r}_i$  have approximately the same value  $\mathbf{r}$  which denotes

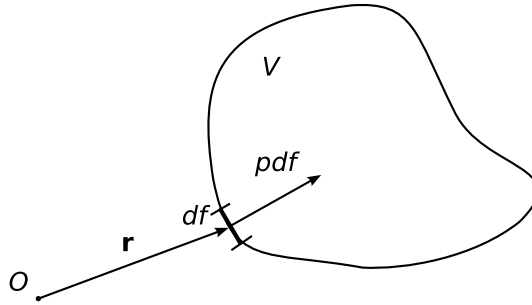


Figure 1: A wall element  $df$  exerts a force  $p df$  on the nearby particles.  $\mathbf{r}$  denotes the vector from the origin to the wall element.

the vector from the origin to the wall element  $df$ . The part of  $df$  to the outer virial can be written as

$$\overline{\sum_{i=1}^N \mathbf{r}_i F_{p,i}} = \overline{\mathbf{r} \sum_{i=1}^N \mathbf{F}_{p,i}} = -\mathbf{r} p df. \quad (25)$$

The outer virial us calculated by integration over the whole surface

$$W_a = -p \int \partial V \mathbf{r} df = -p \int_V \text{div} \mathbf{r} dV = -3pV. \quad (26)$$

Doing the splitting into outer and inner virial in Eq. 24 and solving for the pressure leads to

$$p = \frac{2}{3V} (\Xi - E_{kin}) \quad (27)$$

## References

- [1] Gromacs manual
- [2] H.J.C. Berendsen et al., J. Chem. Phys. **81**, 3684 (1984)
- [3] H.C. Andersen, J. Chem. Phys. **72**, 2384 (1980)
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- [5] S. Nosé and M.L. Klein, Molecular Physics **50**, 1055 (1983)
- [6] R. Becker, Theorie der Wärme, Berlin, Springer (1985)