To obtain a useful expression for calculating pressure we start from Maxwell's expression

$$P = -\frac{\partial A}{\partial \Omega}\bigg|_T$$

where A is the Helmholtz free energy $E - TS = -k_B T \ln Z$. If the Hamiltonian of the system is of the usual type $H(p, q) = K(p) + V(q)$, $\ln Z$ decomposes in a sum $\ln Z_p + \ln Z_q$ where the first addend does not depend on Ω and can be neglected when taking the derivative. Therefore

$$P = k_B T \frac{\partial \ln Z_q}{\partial \Omega} = k_B T \frac{1}{Z_q} \frac{\partial}{\partial \Omega} \int_{\Omega^N} d^{3N} q e^{-\beta V(q)}.$$

Since the integration must be extended over the volume Ω (for each particle, therefore, symbolically, over Ω^N), it is not possible to simply bring the derivative within the integral sign. To eliminate the dependence on the extremes of integration, we scale the coordinates: $s = q\Omega^{-1/3}$, so $d^{3N}q = \Omega^N d^{3N}s$. In this way the integration extends over the unit hypercube $\omega = [0, 1]^{3N}$, constant, and we obtain

$$
\begin{aligned}
P &= k_B T \frac{1}{Z_q} \frac{\partial}{\partial \Omega} \left[\Omega^N \int_\omega d^{3N} s e^{-\beta V(s\Omega^{1/3})} \right] \\
&= k_B T \frac{1}{Z_q} \left[N\Omega^{N-1} \int_\omega d^{3N} s e^{-\beta V(s\Omega^{1/3})} + \Omega^N \int_\omega d^{3N} s \frac{\partial}{\partial \Omega} e^{-\beta V(s\Omega^{1/3})} \right] \\
&= k_B T \frac{\Omega^N}{Z_q} \left[\frac{N}{\Omega} \int_\omega d^{3N} s e^{-\beta V(s\Omega^{1/3})} - \frac{1}{k_B T} \int_\omega d^{3N} s e^{-\beta V(s\Omega^{1/3})} \sum \frac{\partial V}{\partial s} \frac{s}{3\Omega} \right].
\end{aligned}
$$

The sum must be understood to run over all configurational degrees of freedom ($3N$ in total). It has been assumed that the pressure is due exclusively to the interactions between particles; in the case that there is a contribution to the energy U that depends exclusively on the volume of the system (which for example happens in metals) one has simply to add a term equal to $-\frac{\partial U}{\partial \Omega}$.

Returning to the original variables q

$$P = \frac{Nk_B T}{\Omega} - \frac{1}{3\Omega} \left\langle \sum \frac{\partial V}{\partial q} q \right\rangle.$$

The first term is the ideal gas term, the only one that remains even if $V = 0$. The averaged term, up to constants, is called *virial*, and in terms of three-dimensional vectors its expression for point particles is

$$\text{virial} = \left\langle \sum_I \mathbf{F}_I \cdot \mathbf{r}_I \right\rangle$$

where the sum now runs over the particle indices. In the case of two-body forces $\mathbf{F}_{IJ}$, $\mathbf{F}_I = \sum_J \mathbf{F}_{IJ}$, and exploiting Newton's third principle $\mathbf{F}_{JI} = -\mathbf{F}_{IJ}$ to exchange the indices I and J we finally have

$$
\begin{aligned}
P &= \frac{Nk_BT}{\Omega} + \frac{1}{3\Omega}\left\langle \sum_{IJ,I<J} \mathbf{F}_{IJ} \cdot \mathit{bfr}_I + \sum_{IJ,I>J} \mathbf{F}_{IJ} \cdot \mathbf{r}_I \right\rangle \\
&= \frac{Nk_BT}{\Omega} + \frac{1}{3\Omega}\left\langle \sum_{IJ,I<J} \mathbf{F}_{IJ} \cdot \mathbf{r}_I - \sum_{IJ,I<J} \mathbf{F}_{IJ} \cdot \mathbf{r}_J \right\rangle \\
&= \frac{Nk_BT}{\Omega} + \frac{1}{3\Omega}\left\langle \sum_{IJ,I<J} \mathbf{F}_{IJ} \cdot \mathbf{r}_{IJ} \right\rangle, \quad \mathbf{r}_{IJ} = \mathbf{r}_I - \mathbf{r}_J.
\end{aligned}
$$

The virial is a mechanical term that can therefore be calculated through a Molecular Dynamics simulation. In this way one can therefore calculate for example the equation of state of the system.

One may ask whether this result can be used not only to calculate the pressure at constant (N, Ω, E) (microcanonical ensemble), but also in other ensembles, for example the isoenthalpic-isobaric (N, P, H), where H is the enthalpy $H = E + P\Omega$, i.e. if it is possible to carry out a simulation at constant pressure, and not volume. One method was proposed by Andersen.

We start from the Lagrangian of the system, by definition therefore in the microcanonical ensemble:

$$\mathcal{L} = \sum_I \frac{1}{2}m_I \mathbf{v}_I^2 - V(\mathbf{r}).$$

Let's rewrite it by scaling the coordinates $\mathbf{s} = \mathbf{r}\Omega^{-1/3}$, in analogy with what was done before, but making it appear the volume as a variable with a dynamic chosen arbitrarily but appropriately:

$$\mathcal{L} = \sum_I \frac{1}{2}m_I \Omega^{2/3}\dot{\mathbf{s}}_I^2 - V(\Omega^{1/3}\,\mathit{bfs}) + \frac{1}{2}Q\dot{\Omega}^2 - P\Omega.$$

The parameter Q plays here the role of a "mass" of the volume (note, however, that it does not have the dimensions of a mass) and is arbitrary, while P, as we will see immediately, is the desired pressure. The system defined by this new Lagrangian does not have a direct physical meaning, as the dynamics of the volume does not have a physical sense. However this extended system is a perfectly acceptable dynamical system, which describes a conservative dynamics in a fixed volume (for the scaled variables: unit hypercube ω), therefore in a microcanonical ensemble in the space of the new $3N+1$ degrees of freedom. The equations of motion are, using the usual prescriptions of Analytical Mechanics,

$$
\begin{aligned}
m_I \ddot{\mathbf{s}}_I &= \frac{\mathbf{F}_I}{\Omega^{1/3}} - \frac{2}{3}\frac{\dot{\Omega}}{\Omega}\dot{\mathbf{s}}_I \\
Q\ddot{\Omega} &= \sum_I \frac{1}{3\Omega^{1/3}} m_I \dot{\mathbf{s}}_I^2 + \frac{1}{3\Omega^{2/3}}\mathbf{F}_I \cdot \mathbf{s}_I - P \\
&= \frac{2}{3\Omega}\sum_I \frac{1}{2}m_I \dot{\mathbf{r}}_I^2 + \frac{1}{3\Omega}\mathbf{F}_I \cdot \mathbf{r}_I - P.
\end{aligned}
$$

In the second equation the second term on the right is the term which, when averaged, gives the virial. The first instead at equilibrium averages to Nk_BT/Ω, so the second member of the second equation of motion is, when averaged, the pressure exerted by the system minus P. As a result, the volume oscillates in such a way as to maintain the system pressure around P. The crucial point, however, is that it can be shown that the trajectories of the system, once $\mathbf{r}(t) = \Omega^{1/3}\mathbf{s}(t)$, are trajectories that provide the correct averages for a constant pressure system (N, P, H).

We can also define a Hamiltonian

$$
\mathcal{H} = \sum_I \frac{\mathbf{p}_I^2}{2m\Omega^{2/3}} + V(\Omega^{1/3}\mathbf{s}) + \frac{\Pi^2}{2Q} + P\Omega,
$$

($\Pi = Q\dot{\Omega}$ is the conjugated momentum to Ω and $\mathbf{p}_I$ to $\mathbf{s}_I$) which is a constant of motion since it does not explicitly depend on time. This quantity is therefore useful for checking the accuracy of the integration of the equations of motion, thus taking the place of the energy $E = \sum_I \frac{1}{2}m_I\mathbf{v}_I^2 + V(\mathbf{r})$ of the physical system. In fact, the latter is no longer a conserved quantity, since it does not contain the terms of the pseudodynamics of the volume.

The additional equation for Ω can be integrated with the already known methods. The value of Q is in principle irrelevant. However, choosing too high a value for Q leads to a slow dynamics for the volume, which would therefore remain almost constant, making the scheme useless. Too low a value instead gives fast dynamics that overlap with that of particles and could cause disturbances in dynamic quantities, such as correlation functions, or generate unwanted and unphysical resonances. Optimal values are therefore those that give a dynamics for Ω just slower than the slowest modes of the system, for example such that the period of oscillation of Ω is approximately equal to the time that a sound wave takes to pass through the simulation cell.