

# Calculating the Pressure

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## 1 Basics

In standard thermodynamics the pressure  $\mathcal{P}$  is given by the relation

$$\mathcal{P} = - \left( \frac{\partial A}{\partial V} \right)_T \quad (1)$$

where  $A$  is the Helmholtz free energy,  $V$  the volume and  $T$  the temperature. This can be expanded into

$$\mathcal{P} = \frac{1}{\beta} \left( \frac{\partial}{\partial V} \log Q_N(V, T) \right)_T \quad (2)$$

or

$$\mathcal{P} = \frac{1}{\beta Q_N(V, T)} \left( \frac{\partial}{\partial V} Q_N(V, T) \right)_T \quad (3)$$

where  $Q_N(V, T)$  is the partition function

$$Q_N = \frac{1}{N! h^{3N}} \int \int \exp(-\beta H_N(\underline{r}^N, \underline{p}^N)) d\underline{r}^N d\underline{p}^N \quad (4)$$

and  $H_N(\underline{r}^N, \underline{p}^N)$  is the system Hamiltonian (assuming a canonical ensemble).

In order to calculate the pressure from these expressions it is necessary to introduce the scaling relations:

$$\underline{r}_i = V^{1/3} \underline{s}_i, \quad \underline{\pi}_i = V^{2/3} m_i \underline{\dot{s}}_i, \quad \underline{p}_i = V^{-1/3} \underline{\pi}_i, \quad (5)$$

where  $\{\underline{r}_i, \underline{p}_i\}$  and  $\{\underline{s}_i, \underline{\pi}_i\}$  are conjugate pairs of atomic positions and momenta in real and ‘scaled’ space respectively. Use of these relations allows the pressure equation to be written as

$$\begin{aligned} \mathcal{P} = & - \frac{1}{(N! h^{3N} Q_N(V, T))} \int \int \left( \frac{\partial}{\partial V} H_N(V^{1/3} \underline{s}^N, V^{-1/3} \underline{\pi}^N) \right)_T \\ & \times \exp(-\beta H_N(V^{1/3} \underline{s}^N, V^{-1/3} \underline{\pi}^N)) d\underline{s}^N d\underline{\pi}^N \end{aligned} \quad (6)$$

or in other words

$$\mathcal{P} = - \left\langle \left( \frac{\partial}{\partial V} H_N(V^{1/3} \underline{s}^N, V^{-1/3} \underline{\pi}^N) \right)_T \right\rangle \quad (7)$$

which is the fundamental equation of the method.

## 2 Example Applications

### 2.1 Simple Atomic System with Pair forces

The Hamiltonian for such a system is

$$H_N(\underline{r}^N, \underline{p}^N) = \sum_{i=1}^N \frac{p_i^2}{2m_i} + \sum_{i=2}^N \sum_{j<i} U(r_{ij}), \quad (8)$$

where  $r_{ij}$  is the separation between atoms  $i$  and  $j$ . This may be transformed using the scaled variables into

$$H_N(V^{1/3} \underline{s}^N, V^{-1/3} \underline{\pi}^N) = V^{-2/3} \sum_{i=1}^N \frac{\pi_i^2}{2m_i} + \sum_{i=2}^N \sum_{j<i} U(V^{1/3} s_{ij}) \quad (9)$$

It is easy to show that

$$\frac{\partial H_N}{\partial V} = -\frac{2}{3V} V^{-2/3} \sum_{i=1}^N \frac{\pi_i^2}{2m_i} + \frac{1}{3V} V^{1/3} \sum_{i=2}^N \sum_{j<i} U'(V^{1/3} s_{ij}) s_{ij}, \quad (10)$$

where  $U'(x)$  is the first derivative of  $U(x)$  with respect to the argument  $x$ . This relation can be transformed back into the original variables as

$$\frac{\partial H_N}{\partial V} = -\frac{2}{3V} \sum_{i=1}^N \frac{p_i^2}{2m_i} + \frac{1}{3V} \sum_{i=2}^N \sum_{j<i} \frac{1}{r_{ij}} U'(r_{ij}) \underline{r}_{ij} \cdot \underline{r}_{ij}, \quad (11)$$

where the scalar product  $\underline{r}_{ij} \cdot \underline{r}_{ij}$  has been introduced into the second rhs term to bring out the relationship between this term and the usual virial.

The pressure in this system is therefore:

$$\mathcal{P} = \frac{1}{3V} \left\langle 2 \sum_{i=1}^N \frac{p_i^2}{2m_i} - \sum_{i=2}^N \sum_{j<i} \frac{1}{r_{ij}} U'(r_{ij}) \underline{r}_{ij} \cdot \underline{r}_{ij} \right\rangle \quad (12)$$

which is the same as the form given by the virial theorem.

## 2.2 Flexible Polyatomic Molecules

The Hamiltonian for a system of flexible polyatomic molecules (i.e. without constrained bonds and angles *etc*) is commonly of the form:

$$\begin{aligned}
 H_N(\underline{\mathbf{r}}^N, \underline{\mathbf{p}}^N) = & \sum_{i=1}^N \frac{p_i^2}{2m_i} + \sum_{i=2}^N \sum_{j<i} U^{nb}(r_{ij}) + \\
 & \sum_{k=1}^{N_b} U_k^b(r_{ab}) + \sum_{k=1}^{N_t} U_k^t(\underline{\mathbf{r}}_a, \underline{\mathbf{r}}_b, \underline{\mathbf{r}}_c) + \\
 & \sum_{k=1}^{N_f} U_k^f(\underline{\mathbf{r}}_a, \underline{\mathbf{r}}_b, \underline{\mathbf{r}}_c, \underline{\mathbf{r}}_d)
 \end{aligned} \tag{13}$$

Clearly, the kinetic energy, nonbonded terms ( $U^{nb}$ ) and bonded terms  $U_k^b$  may be treated in exactly the same way as the previous case. The three body ( $U_k^t$ ) and four body terms need to be considered on a case-by-case basis.

In dealing with three body terms, three common cases occur:

1.  $U_k^t(r_{ab}, r_{bc}, r_{ac})$ ; the potential depends on three spatial separation between three atoms (e.g. Axilrod-Teller potential). This becomes  $U_k^t(V^{1/3}s_{ab}, V^{1/3}s_{bc}, V^{1/3}s_{ac})$  after the scaling transformation, which on differentiation wrt  $V$  clearly contributes to the virial.
2.  $U_k^t(\hat{r}_{ab}, \hat{r}_{bc})$ ; the potential depends on the relative positions of three atoms, but it is the angles between the vectors that determine the potential (e.g. the valence angle potential). These potentials are unaffected by the scaling transformation and so cannot contribute to the pressure.
3.  $U_k^t(\hat{r}_{ab}, \hat{r}_{bc}) \times S(r_{ab}, r_{bc})$ ; the potential has both an angular part and a ‘switching’ function which zeroes the potential at long range (e.g. the Leslie three body potential). Provided the switching function is analytical, the scaling transformation gives  $U_k^t(\hat{r}_{ab}, \hat{r}_{bc}) \times S(V^{1/3}s_{ab}, V^{1/3}s_{bc})$ , which clearly will contribute to the pressure.

With regard to four body terms, the only common potential (that I am aware of) is the dihedral angle potential:  $U_k^f(\hat{r}_{ab}, \hat{r}_{bc}, \hat{r}_{cd})$ ; which has no dependence on interatomic distance, and hence no contribution to the pressure.

## 2.3 Diatomic Molecule with Extensible Bond

The atomic positions of the  $i$ 'th molecule are given by

$$\underline{\mathbf{R}}_i^a = \underline{\mathbf{R}}_i + \underline{\mathbf{d}}_i^a \quad \underline{\mathbf{R}}_i^b = \underline{\mathbf{R}}_i + \underline{\mathbf{d}}_i^b \tag{14}$$

with

$$\underline{d}_i^a = -\frac{\mu_i}{m_i^a} \underline{B}_i \quad \underline{d}_i^b = \frac{\mu_i}{m_i^b} \underline{B}_i \quad (15)$$

Where  $\underline{R}_i$  locates the molecule COM and  $\underline{B}_i$  is the bond vector. Vectors  $\underline{d}_i^a$  and  $\underline{d}_i^b$  define the positions of atoms  $a$  and  $b$  respectively, wrt the centre of mass.  $m_i^a$  and  $m_i^b$  are atomic masses  $\mu_i$  the reduced mass. (The molecule mass will be designated  $M_i$ .)

The partition function is

$$Q_N(V, T) = \mathcal{N} \int \dots \int \exp(-\beta H_N(\underline{R}^N, \underline{B}^N, \underline{P}^N, \underline{Q}^N)) d\underline{R}^N d\underline{B}^N d\underline{P}^N d\underline{Q}^N, \quad (16)$$

The appropriate scaled (conjugate) coordinates are

$$\underline{R}_i = V^{1/3} \underline{S}_i \quad \underline{\Pi}_i = V^{2/3} M_i \dot{\underline{S}}_i \quad \underline{P}_i = V^{-1/3} \underline{\Pi}_i \quad (17)$$

$$\underline{B}_i = V^{1/3} \underline{D}_i \quad \underline{\Lambda}_i = V^{2/3} \mu_i \dot{\underline{D}}_i \quad \underline{Q}_i = V^{-1/3} \underline{\Lambda}_i \quad (18)$$

The pressure is therefore

$$\mathcal{P} = - \left\langle \left( \frac{\partial}{\partial V} H_N(V^{1/3} \underline{S}^N, V^{1/3} \underline{D}^N, V^{-1/3} \underline{\Pi}^N, V^{-1/3} \underline{\Lambda}^N) \right) \right\rangle_T \quad (19)$$

where, assuming atom-atom pair forces, the Hamiltonian is

$$H_N(V^{1/3} \underline{S}^N, V^{1/3} \underline{D}^N, V^{-1/3} \underline{\Pi}^N, V^{-1/3} \underline{\Lambda}^N) = \quad (20)$$

$$V^{-2/3} \sum_{i=1}^N \frac{\Pi_i^2}{2M_i} + V^{-2/3} \sum_{i=1}^N \frac{\Lambda_i^2}{2\mu_i} + \sum_{i=2}^N \sum_{j<i}^2 \sum_{a=1}^2 \sum_{b=1}^2 U^{nb}(V^{1/3} S_{ij}^{ab}) + \sum_{i=1}^N U^b(V^{1/3} D_i) \quad (21)$$

with

$$\underline{S}_{ij}^{ab} = V^{-1/3} \underline{R}_{ij}^{ab} = V^{-1/3} (\underline{R}_j - \underline{R}_i + \underline{d}_j^b - \underline{d}_i^a) \quad (22)$$

With these formulae it can be shown that

$$\begin{aligned} \mathcal{P} &= \frac{2}{3V} \left\langle \left( V^{-2/3} \sum_{i=1}^N \frac{\Pi_i^2}{2M_i} + V^{-2/3} \sum_{i=1}^N \frac{\Lambda_i^2}{2\mu_i} \right) \right\rangle - \\ &\quad \frac{1}{3V} \left\langle \left( \sum_{i=2}^N \sum_{j<i}^2 V^{1/3} \sum_{a=1}^2 \sum_{b=1}^2 U^{nb}(R_{ij}^{ab}) S_{ij}^{ab} + V^{1/3} \sum_{i=1}^N U^b(B_i) D_i \right) \right\rangle \end{aligned} \quad (23)$$

which is easily reduced to

$$\mathcal{P} = \frac{1}{3V} \left\langle 2 \sum_i^N \left( \frac{P_i^2}{2M_i} + \frac{Q_i^2}{2\mu_i} \right) + \sum_{i=2}^N \sum_{j<i}^2 \sum_{a=1}^2 \sum_{b=1}^2 f_{ij}^{ab} \cdot \underline{R}_{ij}^{ab} + \sum_{i=1}^N f_{ii}^{ab} \cdot \underline{B}_i \right\rangle \quad (24)$$

## Comments

1. Note that the expression for the pressure includes the rotational kinetic energy.

## 2.4 Rigid Diatomic Molecules

The partition function is

$$Q_N(V, T) = \mathcal{N} \int \dots \int \exp(-\beta H_N(\underline{R}^N, \Omega^N, \underline{P}^N, \Lambda^N)) d\underline{R}^N d\Omega^N d\underline{P}^N d\Lambda^N, \quad (25)$$

where  $\Omega^N = (\Theta^N, \Phi^N)$  are the angles defining the molecular orientations and  $\Lambda^N = (\Lambda_\theta^N, \Lambda_\phi^N)$  their respective conjugate momenta. The momenta are given by

$$\underline{P}_i = M_i \dot{\underline{R}}_i, \quad \Lambda_{i\theta} = \mu_i B_i^2 \dot{\Theta}_i, \quad \Lambda_{i\phi} = \mu_i B_i^2 \cos^2(\Theta)_i \dot{\Phi}_i. \quad (26)$$

$B_i$  is the (constant) bondlength of molecule  $i$ .

Using the scaling relation and its conjugate momentum:

$$\underline{R}_i = V^{1/3} \underline{S}_i \quad \underline{\Pi}_i = V^{2/3} M_i \dot{\underline{S}}_i \quad \underline{P}_i = V^{-1/3} \underline{\Pi}_i, \quad (27)$$

the pressure can be written directly as

$$\mathcal{P} = - \left\langle \left( \frac{\partial}{\partial V} H_N(V^{1/3} \underline{S}^N, \Omega^N, V^{-1/3} \underline{\Pi}^N, \Lambda^N) \right)_T \right\rangle. \quad (28)$$

It is obvious that there can be no scaling of the angular coordinates. Assuming all the forces arise from atom-atom interactions and using the relations

$$\underline{R}_i^a = \underline{R}_i + \underline{d}_i^a \quad \underline{R}_i^b = \underline{R}_i + \underline{d}_i^b \quad (29)$$

with

$$\underline{d}_i^a = -\frac{\mu_i}{m_i^a} \underline{B}_i \quad \underline{d}_i^b = \frac{\mu_i}{m_i^b} \underline{B}_i \quad (30)$$

as before, we note that the scaling affects only the centre of mass coordinates:

$$\underline{R}_{ij}^{ab} = V^{1/3} \underline{S}_{ij} + \underline{d}_j^b - \underline{d}_i^a \quad (31)$$

where  $V^{1/3} \underline{S}_{ij} = \underline{R}_{ij}$  is the distance between molecules  $i$  and  $j$  (wrt COM). We can write

$$\mathcal{P} = \frac{1}{3V} \left\langle 2 \sum_{i=1}^N \frac{P_i^2}{2M_i} - \sum_{i=2}^N \sum_{j<i} \sum_{a=1}^2 \sum_{b=1}^2 \frac{1}{R_{ij}^{ab}} U^{mb}(R_{ij}^{ab}) \underline{R}_{ij}^{ab} \cdot \underline{R}_{ij} \right\rangle \quad (32)$$

From equation (31) this may be rewritten as

$$\mathcal{P} = \frac{1}{3V} \left\langle 2 \sum_{i=1}^N \frac{P_i^2}{2M_i} + \sum_{i=2}^N \sum_{j<i} \sum_{a=1}^2 \sum_{b=1}^2 \underline{f}_{ij}^{ab} \cdot \underline{R}_{ij}^{ab} - \sum_{i=1}^N \sum_{a=1}^2 \underline{f}_i^a \cdot \underline{d}_i^a \right\rangle \quad (33)$$

where  $\underline{f}_i^a$  is the force on atom  $a$  of molecule  $i$ .

**Comments**

1. There is now no term corresponding to the rotational kinetic energy in the pressure.
2. The last term rhs is a manifestation of the **constraint force**, which appears as an additional term acting on the atoms to keep them bonded. However is **not** the complete constraint force, which also includes contributions from centripetal forces.
3. The absence of centripetal forces is the reason the rotational kinetic energy term is missing.
4. The appearance of the partial constraint force term implies that it is generally necessary to include the constraint forces in calculating the pressure. If the kinetic energy is evaluated atomistically, it will automatically include the necessary rotational energy.

## 2.5 Rigid Polyatomic Molecules

The partition function is

$$Q_N(V, T) = \mathcal{N} \int \dots \int \exp(-\beta H_N(\underline{R}^N, \Omega^N, \underline{P}^N, \Lambda^N)) d\underline{R}^N d\Omega^N d\underline{P}^N d\Lambda^N, \quad (34)$$

where  $\Omega^N = (\Theta^N, \Phi^N, \Psi^N)$  are the Euler angles defining the molecular orientations and  $\Lambda^N = (\Lambda_\theta^N, \Lambda_\phi^N, \Lambda_\psi^N)$  their respective conjugate momenta.

The scaling relation applies to the position vector and translational momentum:

$$\underline{R}_i = V^{1/3} \underline{S}_i \quad \underline{\Pi}_i = V^{2/3} M_i \dot{\underline{S}}_i \quad \underline{P}_i = V^{-1/3} \underline{\Pi}_i. \quad (35)$$

The pressure is given by

$$\mathcal{P} = - \left\langle \left( \frac{\partial}{\partial V} H_N(V^{1/3} \underline{S}^N, \Omega^N, V^{-1/3} \underline{\Pi}^N, \Lambda^N) \right)_T \right\rangle, \quad (36)$$

where assuming all the forces arise from atom-atom pair interactions, the Hamiltonian is

$$H_N(V^{1/3} \underline{S}^N, \Omega^N, V^{-1/3} \underline{\Pi}^N, \Lambda^N) = \quad (37)$$

$$V^{-2/3} \sum_{i=1}^N \frac{\Pi_i^2}{2M_i} + \frac{1}{2} \sum_{i=1}^N \underline{\omega}_i \cdot \underline{I}_i \cdot \underline{\omega}_i + \sum_{i=2}^N \sum_{j < i} \sum_{a=1}^{n_s} \sum_{b=1}^{n_s} U(R_{ij}^{ab}). \quad (38)$$

In this equation,  $\underline{R}_{ij}^{ab}$  represents the separation vector between atoms  $a$  and  $b$  on molecules  $i$  and  $j$  respectively. i.e.

$$\underline{R}_i^a = \underline{R}_i + \underline{d}_i^a \quad (39)$$

with  $\underline{R}_i$  being the centre of mass and  $\underline{d}_i^a$  being the atomic displacement from the COM. Hence

$$\underline{R}_{ij}^{ab} = \underline{R}_{ij} + \underline{d}_{ij}^{ab} \quad (40)$$

and we note that  $\underline{S}_{ij} = V^{-1/3} \underline{R}_{ij}$  is the scaled distance between molecules  $i$  and  $j$  (wrt COM).

The pressure is therefore

$$\mathcal{P} = \frac{1}{3V} \left\langle 2 \sum_{i=1}^N \frac{P_i^2}{2M_i} - \sum_{i=2}^N \sum_{j<i} \sum_{a=1}^{n_s} \sum_{b=1}^{n_s} \frac{1}{R_{ij}^{ab}} U'^{nb}(R_{ij}^{ab}) \underline{R}_{ij}^{ab} \cdot \underline{R}_{ij} \right\rangle \quad (41)$$

which may be written as

$$\mathcal{P} = \frac{1}{3V} \left\langle 2 \sum_{i=1}^N \frac{P_i^2}{2M_i} + \sum_{i=2}^N \sum_{j<i} \sum_{a=1}^{n_s} \sum_{b=1}^{n_s} \underline{f}_{ij}^{ab} \cdot \underline{R}_{ij}^{ab} - \sum_{i=1}^N \sum_{a=1}^{n_s} \underline{f}_i^a \cdot \underline{d}_i^a \right\rangle \quad (42)$$

where  $\underline{f}_i^a$  is the force on atom  $a$  of molecule  $i$ .

## References

- [1] W. Smith, CCP5 Info. Quart. **26** 43 (1987).