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Efficient calculation of the pressure in the canonical ensemble for inverse power central force models

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The pressure in the canonical ensemble is obtained as a function of the virial sum v [1]:

$$P = kT(N - v/3kT)/V \tag{1}$$

with

$$v = \sum_{i<j}^{N} (\underline{r}_{ij} \cdot \underline{\nabla}_i e_{ij}) \tag{2}$$

where k is the Boltzmann factor, T is the absolute temperature, N is the number of particles in the system, V is the volume, $\underline{r}_{ij}$ is the interparticle vector and e_{ij} is the energy of interaction between particles i and j. In general, calculation of the virial sum requires the calculation of the forces on the particles, a non-negligible amount of extra work (unless the force-biased displacement scheme [2] is used where the forces are also needed anyway) and is thus rarely done. However, if e_{ij} depends only on $|\underline{r}_{ij}|$ (i.e. there is only one interaction center per particle) and the interaction follows an inverse power law (or is a sum of inverse power terms) the contribution of particles i and j to the virial sum can be obtained with negligible extra work, since simple application of the chain rule shows that

$$(\underline{r} \cdot \underline{\nabla}(1/|\underline{r}|)^{n}) = -n/|\underline{r}|^{n}. \tag{3}$$

Thus the calculation of the virial sum in this case require only the separate accumulation of the contributions to the total energy from the various distance powers during the simulation and their multiplication with the corresponding exponent n after the simulation.

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References.

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