CALCULATION OF THE PRESSURE IN MOLECULAR SIMULATIONS FROM VOLUME PERTURBATIONS: SOME PRACTICAL APPLICATIONS[1]

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We consider some technical aspects concerning the calculation of the pressure from molecular simulations by performing volume perturbations [1]. The method is based on the numerical estimate of the change in Helmholtz free energy associated to a small perturbation in which the volume of the system is changed from V to $V + \Delta V$. For a system containing N molecules at temperature T, it can be shown that the pressure can be expressed as

$$P = \frac{kT}{\xi V} \ln \left\langle (1+\xi)^N \exp(-\beta \Delta \mathcal{U} \right\rangle$$

where $\beta = (kT)^{-1}$, and $\Delta \mathcal{U}$ is the change in configurational energy associated with the volume perturbation, here defined by the relative volume change $\xi = \Delta V/V$. The most obvious advantage of using the above expression is that a calculation of the pressure (and related thermodynamic quantities) is possible without having to perform an explicit evaluation of the forces (usual virial route used to calculate the pressure in simulations). For complex molecular models this evaluation —otherwise not needed to generate the trajectory in phase space in a Monte Carlo simulation— may be rather complicated and certainly time consuming.
Applications to the calculation of the pressure tensor in inhomogenous systems are presented [2], as well as extensions of the method to the calculation of the surface tension is such systems [3].

[1] V. I. Harismiadis, J. Vorholz, and A. Z. Panagiotopoulos, J. Chem. Phys. **105**, 8469 (1996).

[2] E. de Miguel and G. Jackson, J. Chem. Phys. (submitted).

[3] G. J. Gloor, G. Jackson, F. J. Blas, and E. de Miguel, J. Chem. Phys. **123**, 134703 (2005).

[1] Oral presentation is requested