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ON THE ISOLATION OF POSSIBLE ARTIFACTS DUE TO CUBIC PERIODIC BOUNDARY CONDITIONS

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Cubic periodic boundary conditions in computer simulations of molecular dynamics may produce artifacts due to imposed O_h symmetry. In this communication, group theoretical statistical mechanics is used to isolate ensemble averages which exist under O_h symmetry but vanish under the $R_h(3)$ symmetry of an ensemble of molecules or atoms at thermodynamic equilibrium. These are artifacts of cubic periodic boundary conditions. This method allows a check on the validity of molecular dynamics computer simulations.

1. Introduction

In this communication, a method is suggested for isolating structural and dynamical artifacts due to cubic periodic boundary conditions (PBC's) in computer simulations. The method is based on the application of group theoretical principles to ensembles of atoms or molecules at thermodynamic equilibrium, assuming that the point group generated by the cubic PBC's is O_h, and that of the ensemble at true thermodynamic equilibrium is $R_h(3)$. It is shown group theoretically that O_h supports higher-order ensemble averages that disappear by symmetry in $R_h(3)$, the "artifact-free" point group. The presence of these extra ensemble averages is an indicator of spurious effects due to cubic PBC's, a check which may be incorporated routinely in a simulation code.

2. Group theoretical statistical mechanics

The point group of an isotropic ensemble of archiral molecules or atoms at thermodynamic equilibrium is the group of all rotations and reflections, $R_h(3)$, whose irreducible representations are $D_g^{(0)},\ldots,D_g^{(n)}$ or $D_u^{(0)},\ldots,D_u^{(n)}$, being positive (g) or negative (u) to parity inversion ($\hat{P}$). The superscripts denote tensor order [1–3], and the totally symmetric irreducible representation (TSR) is $D_g^{(0)}$. An ensemble average such as time correlation function or radial distribution function exists in $R_h(3)$ if its irreducible representation contains at least once [4–10] the TSR $D_g^{(0)}$. Otherwise the ensemble average vanishes for all t.

In a computer simulation, periodic boundary conditions are applied whose symmetry is the cubic O_h in the majority of cases. These PBC's may have a spurious effect on some ensemble averages, because O_h symmetry is lower than R_h (3). In the point group O_h, ensemble averages exist if they contain the TSR A_{1g}. To determine the presence of spurious effects due to the lowering of symmetry by PBC's, we provide the following group theoretical analysis.

2.1. Second-order ensemble averages

These are exemplified by the nine element correlation tensor of linear velocity $\langle \boldsymbol{v}(t)\boldsymbol{v}(0)\rangle$. In $R_h(3)$ its representation is the product

$$D_u^{(1)}D_u^{(1)} = D_g^{(0)} + D_g^{(1)} + D_g^{(2)}, \tag{1}$$

which includes the TSR once. The latter represents the autocorrelation function $\langle \boldsymbol{v}(t)\cdot\boldsymbol{v}(0)\rangle$, which exists in the laboratory frame with isotropic components, each with identical time dependence. This symmetry is not affected by cubic PBC's, because the irreducible representation of $\langle \boldsymbol{v}(t)\boldsymbol{v}(0)\rangle$ in O_h is

$$T_{1u}T_{1u} = A_{1g} + E_g + T_{1g} + T_{2g}, \tag{2}$$

which again contains the TSR only once, indicating the existence of the three diagonals with identical time dependence. *In consequence it is not possible to discern artifacts of cubic pcb's by looking at second-order correlation functions alone.*

2.2. Fourth-order ensemble averages

These are exemplified by the twenty seven scalar elements of the general product $\langle \boldsymbol{vvvv}\rangle$, whose irreducible representation in $R_h(3)$ is

$$\begin{aligned} D_u^{(1)}D_u^{(1)} &= \left(D_g^{(0)} + D_g^{(1)} + D_g^{(2)}\right) \\ &\quad\times\left(D_g^{(0)} + D_g^{(1)} + D_g^{(2)}\right) \\ &= 3D_g^{(0)} + 6D_g^{(1)} + 6D_g^{(2)} + 3D_g^{(3)} + D_g^{(4)}, \end{aligned} \tag{3}$$

containing three occurrences of the TSR. The latter indicate the existence of three types of time correlation function, whose origins are given by the way in which the three TSR's appear from the product (3), i.e. from the component products

$$D_g^{(0)}D_g^{(0)} = D_g^{(0)}, \tag{4a}$$

$$D_g^{(1)}D_g^{(1)} = D_g^{(0)} + D_g^{(1)} + D_g^{(2)}, \tag{4b}$$

$$D_g^{(2)}D_g^{(2)} = D_g^{(0)} + D_g^{(1)} + D_g^{(2)} + D_g^{(3)} + D_g^{(4)} \tag{4c}$$

representing the three types

$$\langle \boldsymbol{v}\cdot\boldsymbol{vv}\cdot\boldsymbol{v}\rangle, \tag{5a}$$

$$\langle \boldsymbol{v}\times\boldsymbol{v}\cdot\boldsymbol{v}\times\boldsymbol{v}\rangle, \tag{5b}$$

$$\langle \boldsymbol{v}\cdot\boldsymbol{vv}^{T}\cdot\boldsymbol{v}^{T}\rangle. \tag{5c}$$

These are the only three *three* types of fourth-order time correlation functions allowed by the point group $R_h(3)$.

The point group O_h on the other hand allows *four* different types of fourth-order correlation function, because the relevant product of representation is

$$\begin{aligned} (T_{1u}T_{1u})(T_{1u}T_{1u}) &= \left(A_{1g} + E_g + T_{1g} + T_{2g}\right) \\ &\quad\otimes\left(A_{1g} + E_g + T_{1g} + T_{2g}\right) \\ &= 4A_{1g} + 3A_{2g} + 7E_g \\ &\quad + 10T_{1g} + 10T_{2g}, \end{aligned} \tag{6}$$

which contains the TSR A_{1g} four times. These are given in the O_h character table notation as from:

$$A_{1g}A_{1g}:\quad (x^2+y^2+z^2)(x^2+y^2+z^2); \tag{7}$$

$$E_gE_g:\quad (x^2-y^2, 2z^2-(x^2+y^2))\times(x^2-y^2, 2z^2-(x^2+y^2)); \tag{8}$$

$$T_{1g}T_{1g}:\quad (R_x, R_y, R_z)(R_x, R_y, R_z); \tag{9}$$

$$T_{2g}T_{2g}:\quad (xy, xz, yz)(xy, xz, yz). \tag{10}$$

The first type is akin to (5a) from $R_h(3)$; the third is akin to (5b) from $R_h^{(3)}$; and type (10) is related to (5c) from $R_h(3)$. However, type (8) in O_h is not allowed in $R_h(3)$, so that if it appears in a computer simulation it is the spurious outcome of cubic periodic boundary conditions.

We, therefore, arrive at the useful conclusion that the indicator of artificial cubic periodicity in this class of fourth-order ensemble average is the type (8). Code for the computation of this type of correlation function can easily be accommodated inside a computer simulation routine as a check for any unwanted influence of cubic PBC's. If this function is below the noise level for two or more independent runs, the effect of PBC's on dynamical quantities is probably negligible

Finally, we mention that this test is not restricted to fourth-order velocity correlation functions, but is equally applicable to other types of ensemble average.

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