Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

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Test of formula

$$D = D_{\mathrm{pbc}} + \frac{2.873kT}{6\pi\eta L}. \tag{1}$$

We performed testing calculations using liquid argon [?] modeled by Lennard-Jones particles ($\epsilon_{\mathrm{LJ}}/k = 119.8$ K, $\sigma = 3.405$ Å) at temperature 143.76 K and density 1344.26 $\mathrm{kg\,m^{-3}}$. The viscosity determined by the Green-Kubo formula was 0.1754 mPa.s, the uncorrected and corrected diffusivities are collected in Table 1. It is seen that the convergence of the corrected values to the thermodynamic limit is much faster than of the uncorrected ones. It looks like that the corrected values slightly overshoot the limit, nevertheless the averaged differences are not distinguishable at the 95% confidence level even if the inaccuracy (a few per cent) of viscosity is not taken into account. We may conclude that including correction (1) considerably reduces systematic finite-size errors in diffusivity.

Table 1: Test of equation (1) for liquid argon. N is the number of atoms, BV denotes the Berendsen thermostat (with ideal-gas correlation time τ) with Verlet integration, NG the Nosé-Hoover thermostat (with time constant τ) with 4-point Gear integrator, and D_{pbc} and D are the uncorrected and corrected diffusivities, respectively. The values in parentheses are estimated standard errors (confidence level 68%) in the units of the last significant digit

N	method	τ/ps	$D_{\mathrm{pbc}}/10^{-9}\mathrm{m^2\,s^{-1}}$	$D/10^{-9}\mathrm{m^2\,s^{-1}}$
250	BV	0.2	4.217(19)	4.954
250	BV	1	4.229(22)	4.966
250	NG	0.2	4.210(21)	4.947
250	NG	1	4.220(22)	4.957
2000	BV	0.2	4.560(12)	4.928
2000	BV	1	4.567(11)	4.935
2000	NG	0.2	4.568(13)	4.936
2000	NG	1	4.578(10)	4.947