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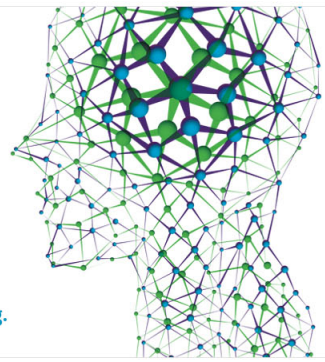

Comment on "Markovian approximation in a coarse-grained description of atomic systems" [J. Chem. Phys. 125, 204101 (2006)]

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The Markovian approximation assumed in particle-based coarse-grained techniques, such as dissipative particle dynamics, was shown to be incorrect for harmonic systems in Refs. 1 and 2. In addition, in Ref. 2, it was presented as a general argument showing that the Markovian approximation is also unreliable in more complex systems in which sound plays an important role. In this context, Hijón *et al.*[3] studied the coarse-graining dynamics of a one-dimensional chain of oscillators interacting through harmonic (linear) and Lennard–Jones (nonlinear) potentials, concluding that the Markovian approximation is appropriate in the latter nonlinear and more realistic system. However, in the nonlinear system analyzed by the authors, the sound plays a very important role, since it determines the time scale of the relevant variables (i.e., the time scale of $\langle P_\nu P_\mu(t)\rangle$). Therefore, these results would be in contradiction with the general argument presented in Ref. 2.

First of all, let us notice that much of the analysis in their work is based on their Eq. (23), which is mathematically incorrect. The reason is that when the Laplace transform of the second equation in their Eq. (9) is taken, instead of Eq. (19), the following equation is obtained:

$$F_\mu(s) = \tilde{F}_\mu(s) - k_B T X^{-1}_{\mu\nu}\left[\frac{X_\nu(0)}{s} + \frac{P_\nu(0)+F_\nu(s)}{nms^2}\right] - \frac{1}{nmk_BTs}\langle \tilde{F}_\nu \tilde{F}_\mu(s)\rangle [F_\nu(s)+P_\nu(0)]. \tag{1}$$

This equation has three extra terms when compared to Eq. (19) from Ref. 3. One of them survives when we multiply this equation by $F_\sigma \equiv F_\sigma(0)$ and average because

$$\langle X_\nu(0)F_\sigma(0)\rangle = -k_BTX^{-1}_{\sigma\nu}\langle X_\nu(0)X_\mu(0)\rangle = -k_BT\delta_{\nu\sigma}. \tag{2}$$

As a result, Eq. (20) from Ref. 3 should be replaced by

$$\tilde{C}(s) = -\frac{(k_BT)^2X^{-1}}{s} + \left[1 - \frac{1}{nmk_BTs}C(s)\right]^{-1}C(s). \tag{3}$$

On the other hand, if we multiply Eq. (9) from Ref. 3 by $P_\sigma(0)$, take averages and the Laplace transform, we arrive to the following equation for $D_{\mu\nu}(s) \equiv \langle P_\mu P_\nu(s)\rangle$:

$$sD(s) - D_0 = -\frac{k_BTX^{-1}D(s)}{nms} - \frac{\tilde{C}(s)}{nmk_BT}D(s), \tag{4}$$

where $D_0 = \langle P(0)P(0)^{\mathrm{T}}\rangle$. Equation (4) is the starting point for the analytical calculation of $\tilde{C}(s)$ in the harmonic case.[2] If we insert Eq. (3) into Eq. (4) and multiply the resulting equation by $[1-(nmk_BT)^{-1}\tilde{C}(s)]$, the following equation is obtained:

$$D(s) = \frac{D_0}{s}\left(1 - \frac{C(s)}{nmk_BTs}\right). \tag{5}$$

Taking the inverse Laplace transform of this equation, we obtain an interesting relation between the correlation of the mesoscopic forces F_μ and momenta P_μ,

$$\langle PP(t)^T\rangle = \langle PP^T\rangle\left(1 - \int_0^t d\tau \int_0^\tau d\tau' \frac{\langle FF(\tau')^T\rangle}{nmk_BT}\right), \tag{6}$$

or, equivalently, since $\langle P_\mu P_\nu\rangle = \delta_{\mu\nu}\langle P_\mu P_\mu\rangle$,

$$\frac{\langle F_\mu F_\nu(t)\rangle}{k_BT} = -(nm)\frac{d^2}{dt^2}\frac{\langle P_\mu P_\nu(t)\rangle}{\langle P_\mu P_\mu\rangle}. \tag{7}$$

This is an exact and novel equation that will be used later on.

My second comment is related to a general procedure used by the authors systematically throughout the paper, which is the neglect of all contributions in the memory kernels which go as $1/n$ in the limit of large cluster sizes ($n \gg 1$). This is a mistaken approach that leads them to conclude that the dynamics is Markovian. To show that these contributions cannot be neglected in the cases they have studied, let us consider the equation of motion for the mesoscopic variables, Eq. (9) from Ref. 3, in terms of the time scale of the relevant variables. As observed in the simulations and repeatedly stated by the authors, this mesoscopic time scale grows linearly with n as the clusters become larger. Therefore, in terms of $t^* = t/n$, we have

$$\frac{1}{n}\frac{dP_\mu}{dt^*} = -\int_0^{t^*} d\tilde{u}\frac{\tilde{C}_{\mu\nu}(nt^* - n\tilde{u})}{mk_BT}P_\nu(n\tilde{u}) - k_BTX^{-1}_{\mu\nu}X_\nu + \tilde{F}_\mu. \tag{8}$$

By comparing the first term in the right-hand side of Eq. (8) with the term in the left-hand side, it is clear that any contribution in the memory kernel $\tilde{C}$ which goes as $1/n$ is of the same order as the rate of change of the momentum and, thus, does contribute to the dynamics at the mesoscopic time scale.

Moreover, we can use Eq. (7) to show that, in the cases studied in the paper, the correlation of forces $C_{\mu\nu}(t) = \langle F_\mu F_\nu(t)\rangle$ is also of order $1/n$. By changing to t^* in Eq. (7), we obtain

$$\frac{\langle F_\mu F_\nu(t)\rangle}{k_B T} = -\frac{m}{n}\frac{d^2}{dt^{*2}}\frac{\langle P_\mu P_\nu(t)\rangle}{\langle P_\mu P_\mu\rangle}. \tag{9}$$

In the two systems analyzed by the authors, the autocorrelation of momenta is seen to obey the following scaling law in the limit of large n:

$$\frac{\langle P_\mu P_\nu(t)\rangle}{\langle P_\mu P_\mu\rangle} = D^*_{\mu\nu}(t^*), \tag{10}$$

where $D^*_{\mu\nu}(t^*)$ is a function of t^* which does not depend on n. This scaling is confirmed by the analytical expression for $D(t)$ in the harmonic case.[2] For the nonlinear system studied by the authors, it can be clearly observed in Fig. 6 of Ref. 3 that their simulation data follows this behavior very well. Thus, from Eqs. (9) and (10), we conclude that $C(t)$ is of order $1/n$. More specifically, it demonstrates that the force correlation has the asymptotic form

$$C(t) = \frac{1}{n}C^*(t^*), \tag{11}$$

where $C^*(t)$ is a matrix independent of n.

Furthermore, it can be shown that all contributions to the memory kernel $\tilde{C}(t)$ present the same behavior, being indeed of order $1/n$. Using Eq. (3), the formal expansion suggested by the authors,

$$\left[1 - \frac{1}{nmk_BTs}C(s)\right]^{-1} = \sum_{l\geq 0}\left[\frac{C(s)}{nmk_BTs}\right]^l, \tag{12}$$

and taking the inverse Laplace transform, we arrive to

$$\tilde{C}(t) = C(t) - k_BTX^{-1} + (C*\Gamma)(t) + (C*\Gamma*\Gamma)(t) + (C*\Gamma*\Gamma*\Gamma)(t) + \cdots, \tag{13}$$

where $(f*g)(t)=\int_0^t d\tau f(\tau)g(t-\tau)$ denotes the convolution and $\Gamma(t)=\int_0^t d\tau C(\tau)/(nmk_BT)$. Equation (13) is the corrected version of Eq. (23) from Ref. 3.

From Eq. (11), it follows that $\Gamma(t)=(1/n)\Gamma^*(t^*)$, where $\Gamma^*(t^*)=\int_0^{t^*} d\tau C^*(\tau)/(mk_BT)$ is independent of n. By using a similar procedure, it is easily seen that each term in Eq. (13) involving $C(t)$ is of order $1/n$. An important consequence is that, in contrast to what is suggested by the authors, we are not entitled to retain only the first two terms of the expansion in Eq. (12) [neither, equivalently, the first three terms in the right-hand side of Eq. (13)]. In addition, the analytical expression for k_BTX^{-1} in the harmonic case[2] shows that this term is of order $1/n$ as well.

Finally, let us further analyze the simulation data of the nonlinear system studied by the authors by making use of Eq. (7). First of all, it is convenient to clarify the behavior of $C^*(t^*)$ in the limit of $t^*\to 0^+$. From Eq. (1), it follows that $d\langle P_\mu P_\nu(t)\rangle/dt=0$ at $t=0$. Thus, integrating Eq. (7) between 0 and $t=n\varepsilon$, with $\varepsilon>0$, and changing to t^*, we arrive to

$$\int_0^\varepsilon dt^* C^*(t^*) = -m\frac{dD^*(\varepsilon)}{dt^*}, \tag{14}$$

which shows that $C^*(t^*)$ [and, thus, $\tilde{C}^*(t^*)$] contains at $t^*=0^+$ the Dirac-delta term $-m[dD^*(0)/dt^*]\delta(t^*-0^+)$. This singular term would be the only nonvanishing contribution expected from $C^*(t^*)$ if the coarse-grained dynamics were Markovian. However, Figs. 4 and 5 in Ref. 3 show that there is an appreciable contribution at later times of the matrix elements of $nC(t)=C^*(t^*)$. This suggests that the memory kernels are nonvanishing and, thus, the coarse-grained dynamics is non-Markovian.

In conclusion, by correcting a few mathematical errors and deriving a new expression for the correlation of forces and momenta, it is shown that it cannot be claimed that the coarse-grained dynamics of the nonlinear system studied by the authors is Markovian. This result is not unexpected because, for the systems analyzed by the authors, the correlation of momenta indicates that the sound plays a very important role in determining the time scale of the mesoscopic variables. In principle, if we increase further and further the size of the clusters in a nonlinear system, we should reach a limit in which sound is strongly damped and the dynamics of the coarse-grained variables is not affected by sound propagation. The dynamics could then be assumed to be Markovian in good approximation, with the same level of accuracy it holds for a classic Brownian particle with a large mass in a fluid. However, this situation corresponds to a drastic macroscopic limit which might be useless in most practical purposes in which the size of the desired coarse-grained description comes determined beforehand. This problem shows that it is very important to check how reliable a coarse-grained technique actually is by studying in detail the validity of the approximations taken at the microscopic level.

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