Coupling a nano-particle with fluctuating hydrodynamics

Aleksandar Donev

Courant Institute, *New York University*
&
Pep Español, *UNED, Madrid, Spain*

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Levels of Coarse-Graining

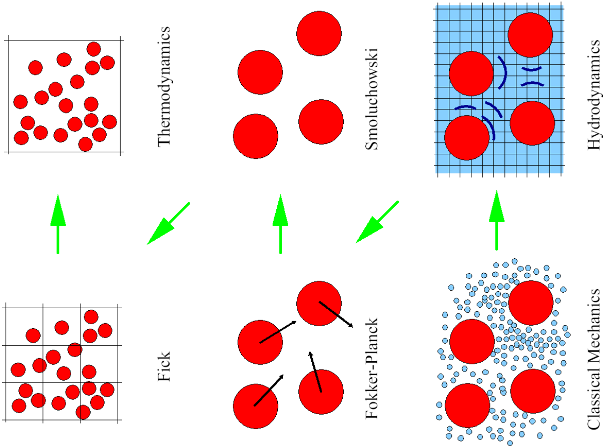


Figure : From Pep Español, "Statistical Mechanics of Coarse-Graining".

Velocity Autocorrelation Function

- Key is the **velocity autocorrelation function** (VACF) for the immersed particle

$$C(t) = \langle \mathbf{V}(t_0) \cdot \mathbf{V}(t_0 + t) \rangle$$

- From equipartition theorem $C(0) = \left\langle V^2 \right\rangle = d\, k_B T / M$ for a compressible fluid, but for an incompressible fluid the kinetic energy of the particle that is **less than equipartition**.
- Hydrodynamic persistence (conservation) gives a **long-time power-law tail** $C(t) \sim (k_B T/M)(t/t_{\text{visc}})^{-3/2}$.
- Diffusion coefficient is given by the **integral of the VACF** and is hard to compute in MD even for a single nanocolloidal particle.

Brownian Bead

- Classical picture for the following dissipation process: *Push a sphere suspended in a liquid with initial velocity* $V_{th} \approx \sqrt{k_B T/M}$ *and watch how the velocity decays:*
  - **Sound waves** are generated from the sudden compression of the fluid and they take away a fraction of the kinetic energy during a **sonic time** $t_{sonic} \approx a/c$, where c is the (adiabatic) sound speed.
  - **Viscous dissipation** then takes over and slows the particle *non-exponentially* over a **viscous time** $t_{visc} \approx \rho a^2/\eta$, where η is the shear viscosity.
  - **Thermal fluctuations** get similarly dissipated, but their constant presence pushes the particle diffusively over a **diffusion time** $t_{diff} \approx a^2/D$, where

$$D \sim k_B T/(a\eta) \quad \text{(Stokes-Einstein relation).}$$

Timescale Estimates

- The mean collision time is $t_{coll} \approx \lambda / V_{th} \sim \eta / (\rho c^2)$,

$$t_{coll} \sim 10^{-15} s = 1 fs$$

- The **sound time**

$$t_{sonic} \sim \begin{cases} 1ns \text{ for } a \sim \mu m \\ 1ps \text{ for } a \sim nm \end{cases}, \text{ with gap } \frac{t_{sonic}}{t_{coll}} \sim 10^2 - 10^5$$

- It is often said that sound waves do not contribute to the long-time diffusive dynamics because their contribution to the VACF integrates to zero.

Estimates contd...

- **Viscous time** estimates

$$t_{visc} \sim \begin{cases} 1\mu s \text{ for } a \sim \mu m \\ 1ps \text{ for } a \sim nm \end{cases}, \text{ with gap } \frac{t_{visc}}{t_{sonic}} \sim 1 - 10^3$$

- Finally, the **diffusion time** can be estimated to be

$$t_{diff} \sim \begin{cases} 1s \text{ for } a \sim \mu m \\ 1ns \text{ for } a \sim nm \end{cases}, \text{ with gap } \frac{t_{diff}}{t_{visc}} \sim 10^3 - 10^6$$

  which can now reach **macroscopic timescales**!

- In practice the **Schmidt number** is very large,

$$Sc = \nu/D = t_{diff}/t_{visc} \gg 1,$$

  which means the diffusive dynamics is **overdamped**.

Brownian Dynamics

- Overdamped equations of **Brownian Dynamics** (BD) for the particle positions $\mathbf{R}(t)$ are

$$\frac{d\mathbf{R}}{dt} = \mathcal{M}\mathbf{F} + (2k_B T \mathcal{M})^{\frac{1}{2}} \, \mathcal{W}(t) + k_B T \, (\partial_{\mathbf{R}} \cdot \mathcal{M}), \tag{1}$$

  where $\mathcal{M}(\mathbf{R}) \succeq \mathbf{0}$ is the symmetric positive semidefinite (SPD) **hydrodynamic mobility matrix**.
- Hydrodynamic mobility matrix is given by Green-Kubo formula

$$(k_B T) \mathcal{M}_{ij} = \int_0^\tau dt \, \langle \mathbf{V}_i(0) \cdot \mathbf{V}_j(t) \rangle^{\text{eq}} . \tag{2}$$

- The upper bound τ must satisfy

$$\tau \gg \frac{r_{ij}^2}{\nu} \sim \frac{L^2}{\nu} \gg t_{visc},$$

  so that the whole VACF power law tail is included in the integral. **Therefore computing hydrodynamic interactions is infeasible with MD.**

Hydrodynamic Diffusion Tensor

- Since computing the hydrodynamic mobility is so difficult in MD, usually $\boldsymbol{\mathcal{M}}$ is modeled by the **Rotne-Prager mobility** [1],

$$\boldsymbol{\mathcal{M}}_{ij} \approx \eta^{-1} \left(\mathbf{I} + \frac{a^2}{6} \boldsymbol{\nabla}^2_{\mathbf{r}} \right) \left(\mathbf{I} + \frac{a^2}{6} \boldsymbol{\nabla}^2_{\mathbf{r}'} \right) \mathbf{G}(\mathbf{r} - \mathbf{r}') \Big|_{\mathbf{r}'=\mathbf{q}_i}^{\mathbf{r}=\mathbf{q}_j}.$$

  where $\mathbf{G}$ is the Green's function for the Stokes problem (**Oseen tensor** for infinite domain).

- This is not only an approximate closure neglecting a number of effects, but also requires an estimate of the effective hydrodynamic radius a as input.
- Our goal will be to split the integral into a short-time piece, computed by **feasible** MD via Green-Kubo integrals, and a long-time contribution, computed by fluctuating hydrodynamics coupled to an immersed particle.

"Old" approach: Particle/Continuum Hybrid

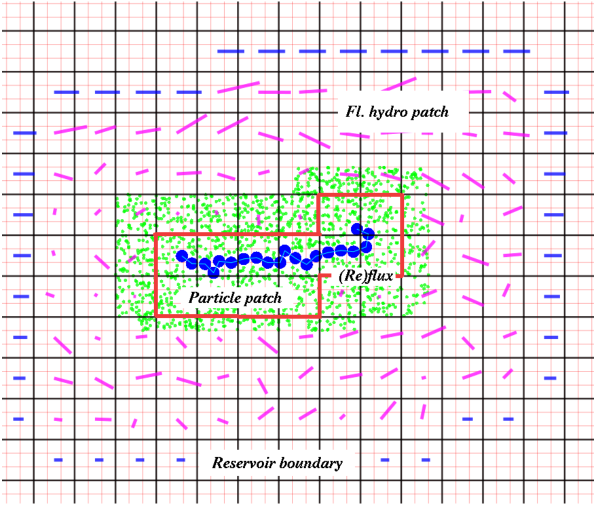
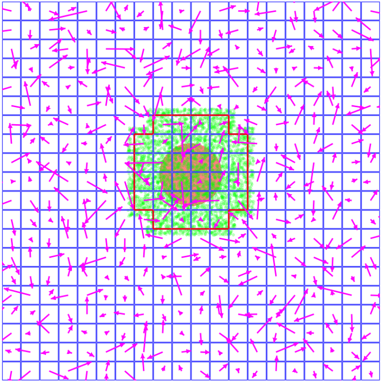


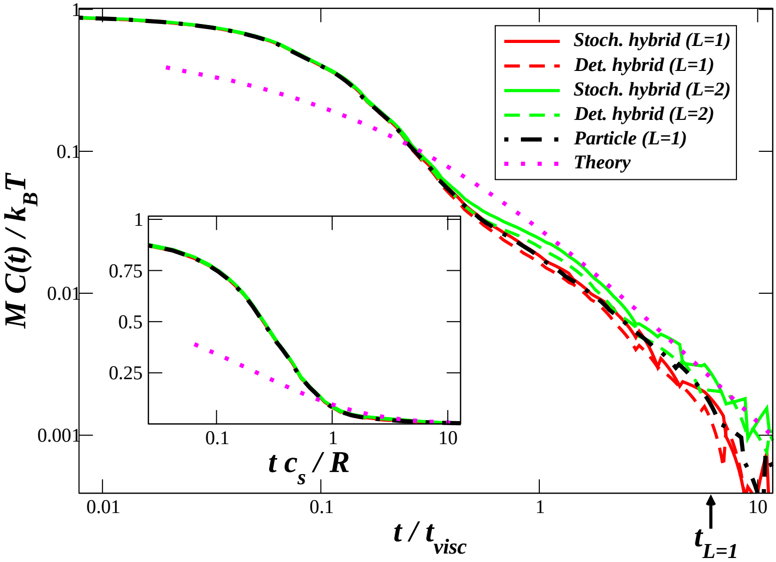
Figure : Hybrid method for a polymer chain.

VACF using a hybrid

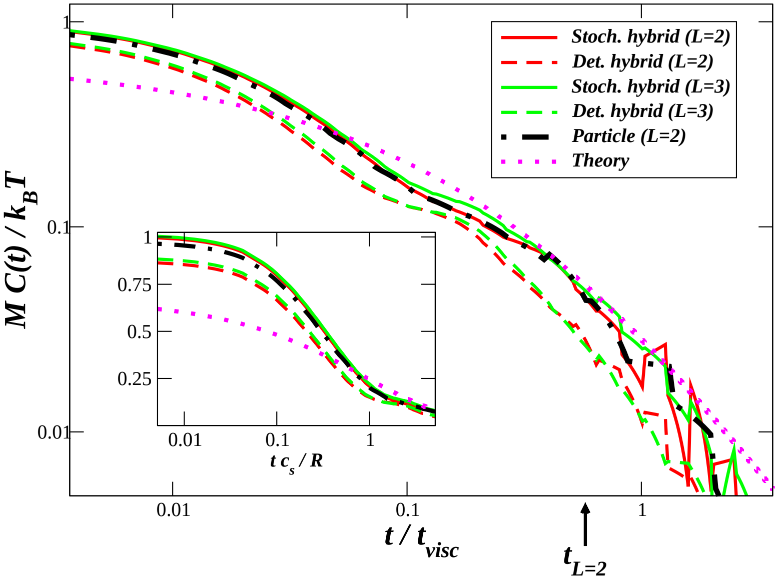


- Split the domain into a **particle** and a **continuum (hydro) subdomains** [2].
- Particle solver is a coarse-grained fluid model (**Isotropic DSMC**).
- Hydro solver is a simple explicit **(fluctuating) compressible fluctuating hydrodynamics** code.
- **Time scales are limited by the MD** part despite increased efficiency.

Small Bead (~10 particles)



Large Bead (~1000 particles)



New Approach: Fluctuating Hydrodynamics

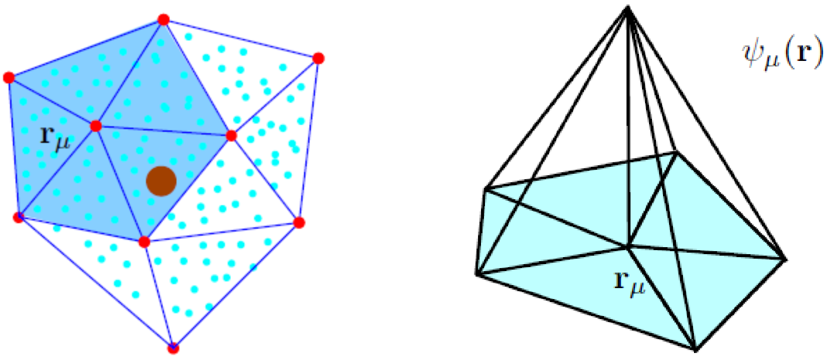


Figure : **Coarse-Graining a Nanoparticle**: Schematic representation of a nanoparticle (left) surrounded by molecules of a simple liquid solvent (in blue). The shaded area around node μ located at $\mathbf{r}_\mu$ is the support of the finite element function $\psi_\mu(\mathbf{r})$ and defines the hydrodynamic cell (right).

Notation

- Define an orthogonal set of basis functions,

$$\|\delta_\mu \psi_\nu\| = \delta_{\mu\nu}, \tag{3}$$

where $\|f\| \equiv \int d\mathbf{r} f(\mathbf{r})$.
- Continuum fields which are interpolated from discrete "fields":

$$\overline{\rho}(\mathbf{r}) = \psi_\mu(\mathbf{r})\rho_\mu \tag{4}$$

- Introduce a *regularized* Dirac delta function

$$\Delta(\mathbf{r}, \mathbf{r}') \equiv \delta_\mu(\mathbf{r})\psi_\mu(\mathbf{r}') = \Delta(\mathbf{r}', \mathbf{r}) \tag{5}$$

- Note the exact properties

$$\int d\mathbf{r}\delta_\mu(\mathbf{r}) = 1, \quad \int d\mathbf{r}\ \mathbf{r}\delta_\mu(\mathbf{r}) = \mathbf{r}_\mu \tag{6}$$

$$\int d\mathbf{r}' \Delta(\mathbf{r}, \mathbf{r}')\delta_\mu(\mathbf{r}') = \delta_\mu(\mathbf{r})$$

Slow variables

- Key to the Theory of Coarse-Graining is the proper selection of the relevant or **slow variables**.
- We assume that the **nanoparticle is smaller than hydrodynamic cells** and accordingly choose the coarse-grained variables [3],

$$\hat{\mathbf{R}}\left(z=\{\mathbf{q},\mathbf{p}\}\right)=\mathbf{q}_0, \tag{7}$$

- We define the mass and momentum densities of the **hydrodynamic node** μ according to

$$\hat{\rho}_\mu(z)=\sum_{i=0}^{N} m_i\delta_\mu(\mathbf{q}_i),\quad \text{discrete of}\quad \hat{\rho}_\mathbf{r}(z)=\sum_{i=0}^{N} m_i\delta(\mathbf{q}_i-\mathbf{r})$$

$$\hat{\mathbf{g}}_\mu(z)=\sum_{i=0}^{N} \mathbf{p}_i\delta_\mu(\mathbf{q}_i),\quad \text{discrete of}\quad \hat{\mathbf{g}}_\mathbf{r}(z)=\sum_{i=0}^{N} \mathbf{p}_i\delta(\mathbf{q}_i-\mathbf{r})$$

where $i=0$ labels the nanoparticle. Note that both mass and momentum densities **include the nanoparticle**!

$$\frac{d\mathbf{R}}{dt} = \bar{\mathbf{v}}(\mathbf{R}) - \frac{D_0}{k_B T}\frac{\partial \mathcal{F}}{\partial \mathbf{R}} + \frac{D_0}{k_B T}\mathbf{F}^{\text{ext}} + \sqrt{2k_B T D_0}\,\mathcal{W}(t)$$

$$\frac{d\rho_\mu}{dt} = \|\overline{\rho}\,\bar{\mathbf{v}}\cdot\boldsymbol{\nabla}\delta_\mu\|$$

$$\frac{d\mathbf{g}_\mu}{dt} = \|\overline{\mathbf{g}}\,\bar{\mathbf{v}}\cdot\boldsymbol{\nabla}\delta_\mu\| + k_B T\boldsymbol{\nabla}\delta_\mu(\mathbf{R}) - \|\delta_\mu\boldsymbol{\nabla}P\| + \delta_\mu(\mathbf{R})\mathbf{F}^{\text{ext}}$$

$$+ \eta\|\delta_\mu\nabla^2\bar{\mathbf{v}}\| + \left(\frac{\eta}{3}+\zeta\right)\|\delta_\mu\boldsymbol{\nabla}\left(\boldsymbol{\nabla}\cdot\bar{\mathbf{v}}\right)\| + \frac{d\tilde{\mathbf{g}}_\mu}{dt} \quad (8)$$

The pressure equation of state is *modeled* by

$$P(\mathbf{r}) \simeq \frac{c^2}{2\rho_{\text{eq}}}\left(\overline{\rho}(\mathbf{r})^2 - \rho_{\text{eq}}^2\right) + m_0\frac{(c_0^2 - c^2)}{\rho_{\text{eq}}}\Delta(\mathbf{R},\mathbf{r})\overline{\rho}(\mathbf{r}), \quad (9)$$

and the gradient of the free energy is *modeled* by

$$\frac{\partial \mathcal{F}}{\partial \mathbf{R}} \simeq m_0\frac{(c_0^2 - c^2)}{\rho_{\text{eq}}}\int d\mathbf{r}\Delta(\mathbf{R},\mathbf{r})\boldsymbol{\nabla}\overline{\rho}(\mathbf{r}). \quad (10)$$

Final Continuum Equations

The same equations can be obtained from a Petrov-Galerkin discretization of the following system of the fluctuating hydrodynamics SPDEs

$$
\begin{aligned}
\frac{d}{dt}\mathbf{R} &= \int d\mathbf{r}\Delta(\mathbf{r},\mathbf{R})\mathbf{v}(\mathbf{r}) + \frac{D_0}{k_B T}\mathbf{F}^{\mathrm{ext}} + \sqrt{2k_B T D_0}\,\boldsymbol{\mathcal{W}}(t) \\
&\quad - \frac{D_0}{k_B T}\frac{m_0(c_0^2 - c^2)}{\rho_{\mathrm{eq}}}\int d\mathbf{r}\Delta(\mathbf{R},\mathbf{r})\boldsymbol{\nabla}\rho(\mathbf{r}) \\
\partial_t\rho(\mathbf{r},t) &= -\boldsymbol{\nabla}\cdot\mathbf{g} \\
\partial_t\mathbf{g}(\mathbf{r},t) &= -\boldsymbol{\nabla}\cdot(\mathbf{g}\mathbf{v}) - k_B T\boldsymbol{\nabla}\Delta(\mathbf{r},\mathbf{R}) \\
&\quad - \boldsymbol{\nabla}P(\mathbf{r}) + \mathbf{F}^{\mathrm{ext}}\Delta(\mathbf{r},\mathbf{R}) \\
&\quad + \eta\nabla^2\mathbf{v} + \left(\frac{\eta}{3} + \zeta\right)\boldsymbol{\nabla}\left(\boldsymbol{\nabla}\cdot\mathbf{v}\right) + \boldsymbol{\nabla}\cdot\boldsymbol{\Sigma}_{\mathbf{r}}^{\alpha\beta} \qquad (11)
\end{aligned}
$$

where $\mathbf{v} = \mathbf{g}/\rho$, and the pressure is given by

$$
P(\mathbf{r}) = \frac{c^2}{2\rho_{\mathrm{eq}}}\left(\rho(\mathbf{r})^2 - \rho_{\mathrm{eq}}^2\right) + \frac{m_0(c_0^2 - c^2)}{\rho_{\mathrm{eq}}}\Delta(\mathbf{R},\mathbf{r})\rho(\mathbf{r}) \qquad (12)
$$

Diffusion Coefficient

- The scalar **bare diffusion coefficient is grid-dependent**,

$$D_0 = \frac{1}{d} \int_0^{\tau} dt \left\langle \delta\hat{\mathbf{V}}(0) \cdot \delta\hat{\mathbf{V}}(t) \right\rangle_{\mathrm{eq}} \tag{13}$$

where the particle **excess velocity** over the fluid is

$$\delta\hat{\mathbf{V}} = \hat{\mathbf{V}} - \left\langle \hat{\mathbf{V}} \right\rangle^{\hat{\mathbf{R}}\hat{\rho}\hat{\mathbf{g}}} \approx \hat{\mathbf{V}} - \bar{\mathbf{v}}(\mathbf{R}).$$

- The crucial point is that now the integration time $\tau \gg h^2/\nu$, where h is the grid spacing, is **accessible in MD**.
- The true or **renormalized diffusion coefficient** [4] *should* be **grid-independent**,

$$D = D_0 + \Delta D \approx D_0 + \frac{1}{d} \int_0^{\tau} dt \left\langle \bar{\mathbf{v}}(\mathbf{R}(0)) \cdot \bar{\mathbf{v}}(\mathbf{R}(t)) \right\rangle^{\mathrm{eq}}$$

$$\approx D_0 + \frac{1}{d} \int_0^{\infty} dt \, \psi_\mu(\mathbf{R}) \left\langle \mathbf{v}_\mu(0) \cdot \mathbf{v}_{\mu'}(t) \right\rangle_{\mathbf{R}}^{\mathrm{eq}} \psi_{\mu'}(\mathbf{R})$$

Numerical VACF

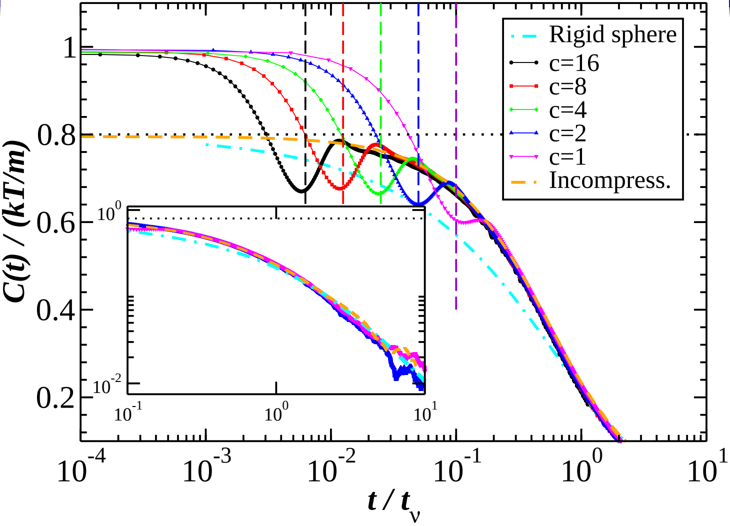


Figure : VACF for a neutrally buoyant particle for $D_0 = 0$ and $c = c_0$, from coupling a **finite-volume** fluctuating hydrodynamic solver [5, 6].

Conclusions

- We considered the problem of modeling the Brownian motion of a solvated nanocolloidal particle over a range of time scales.
- Hydrodynamic scales are not accessible in direct MD so **coarse-grained models are necessary**.
- If one eliminates the solvent DOFs one obtains a *long-memory non-Markovian* SDE in the inertial case or a *long-ranged* overdamped SDE in the Brownian limit.
- If **fluctuating hydrodynamic variables** are retained in the description, one obtains a *large system of Markovian S(P)DEs*.
- A concurrent **hybrid coupling approach** couples MD directly to fluctuating hydrodynamics; **time scales are limited by the MD**.
- We derive coarse-grained equations by a combination of Mori-Zwanzig with physically-informed modeling.
- It remains to actually **try this in practice** and see what range of effects can be captured correctly and efficiently.
  It also remains to generalize this to a **denser suspension of colloids**.

References

S. Delong, F. Balboa Usabiaga, R. Delgado-Buscalioni, B. E. Griffith, and A. Donev.
Brownian Dynamics without Green's Functions.
J. Chem. Phys., 140(13):134110, 2014.
Software available at `https://github.com/stochasticHydroTools/FIB`.

A. Donev, J. B. Bell, A. L. Garcia, and B. J. Alder.
A hybrid particle-continuum method for hydrodynamics of complex fluids.
SIAM J. Multiscale Modeling and Simulation, 8(3):871–911, 2010.

P. Español and A. Donev.
Coupling a nano-particle with isothermal fluctuating hydrodynamics: Coarse-graining from microscopic to mesoscopic dynamics.
J. Chem. Phys., 143(23), 2015.

A. Donev, T. G. Fai, and E. Vanden-Eijnden.
A reversible mesoscopic model of diffusion in liquids: from giant fluctuations to Fick's law.
Journal of Statistical Mechanics: Theory and Experiment, 2014(4):P04004, 2014.

F. Balboa Usabiaga, R. Delgado-Buscalioni, B. E. Griffith, and A. Donev.
Inertial Coupling Method for particles in an incompressible fluctuating fluid.
Comput. Methods Appl. Mech. Engrg., 269:139–172, 2014.
Code available at `https://github.com/fbusabiaga/fluam`.

F. Balboa Usabiaga, X. Xie, R. Delgado-Buscalioni, and A. Donev.
The Stokes-Einstein Relation at Moderate Schmidt Number.
J. Chem. Phys., 139(21):214113, 2013.