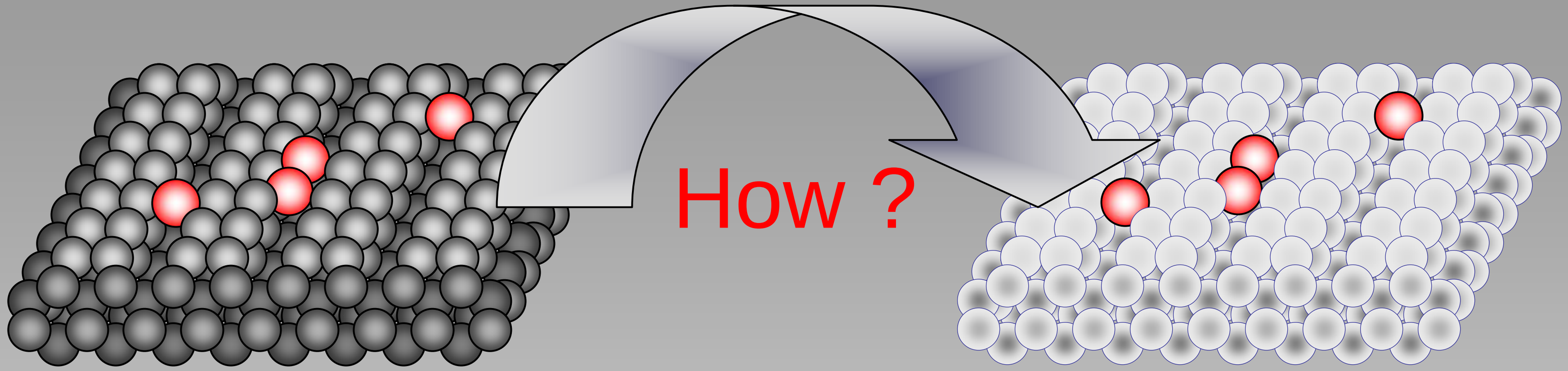
Langevin equation for a system nonlinearly coupled to a heat bath

Mykhaylo Evstigneev

BEMOD 12
MPIPKS, Dresden
March 27, 2012

Motivation

- Molecular dynamics:
- Stochastic dynamics:



10^N atoms of the heat bath,
$N < 10$

n atoms of the system,
$n \sim 1 \ldots 10$

Equations of motion:

system: $\dot{p}_\alpha = f_\alpha(\mathbf{x}) + F_\alpha(\mathbf{x},\mathbf{X})$

bath: $\dot{P}_\mu = g_\mu(\mathbf{X}) + G_\mu(\mathbf{x},\mathbf{X})$

atoms of the heat bath
not simulated explicitly

Langevin equations of motion:

$$\dot{p}_\alpha = \tilde{f}_\alpha(\mathbf{x}) - \eta_{\alpha\beta}(\mathbf{x})\dot{x}_\beta + \xi_\alpha(\mathbf{x}_t, t)$$

Forces:

- renormalized
- dissipative
- random

Langevin simulation

- Langevin equation $$\dot{p}_\alpha = \tilde{f}_\alpha(\mathbf{x}_t) - \eta_{\alpha\beta}(\mathbf{x}_t)\dot{x}_\beta(t) + \xi_\alpha(\mathbf{x}_t, t)$$
- Noise
  - Unbiased: $$\langle \xi_\alpha(\mathbf{x}_t, t) \rangle = 0$$
  - Gaussian and white: $$\langle \xi_\alpha(\mathbf{x}_t, t)\, \xi_\beta(\mathbf{x}_s, s) \rangle = 2k_B T\, \eta_{\alpha\beta}(\mathbf{x}_t)\, \delta(t-s)$$
- Implementation: $$m_\alpha \frac{v_\alpha^{[n+1/2]} - v_\alpha^{[n-1/2]}}{\Delta t} = \tilde{f}_\alpha(\mathbf{x}^{[n]}) - \eta_{\alpha\beta}(\mathbf{x}^{[n-1]}) v_\beta^{[n-1/2]} + r_\alpha^{[n]}$$

$$x_\alpha^{[n+1]} = x_\alpha^{[n]} + v_\alpha^{[n+1/2]}\, \Delta t$$

with Gaussian random numbers $r_\alpha^{[n]}$ having the statistical properties:

$$\langle r_\alpha^{[n]} \rangle = 0 \; ; \; \langle r_\alpha^{[n]}\, r_\beta^{[k]} \rangle = 2k_B T\, \eta_{\alpha\beta}(\mathbf{x}^{[n]})\, \delta_{nk} / \Delta t$$

Plan of the derivation

- Step 1. From the heat bath equations of motion

$$\dot{P}_\mu = g_\mu(\mathbf{X}) + G_\mu(\mathbf{x}, \mathbf{X})$$

approximately evaluate

$$X_\mu(t) \cong \overline{X}_\mu([\mathbf{x}(t' < t)]) + u_\mu(t)$$

(systematic part + noise)

- Step 2. Plug the result back into the system's equations of motion:

$$\dot{p}_\alpha = f_\alpha(\mathbf{x}) + F_\alpha(\mathbf{x}, \mathbf{X}) \cong f_\alpha(\mathbf{x}) + F_\alpha\left(\mathbf{x}, \overline{\mathbf{X}}([\mathbf{x}]) + \mathbf{u}(t)\right)$$

- Step 3. Linearize $F_\alpha\left(\mathbf{x}, \overline{\mathbf{X}}([\mathbf{x}], t) + \mathbf{u}(t)\right)$ to single out force renormalization, dissipation, and noise effects

- Step 4. Take the limit of zero noise correlation time

Standard recipe

- Initial microscopic equations:

$$\dot{p}_\alpha = f_\alpha(\mathbf{x}) + F_\alpha(\mathbf{x},\mathbf{X}); \qquad \dot{P}_\mu = g_\mu(\mathbf{X}) + G_\mu(\mathbf{x},\mathbf{X})$$

- Langevin equation: $\dot{p}_\alpha = \tilde{f}_\alpha(\mathbf{x}) - \eta_{\alpha\beta}(\mathbf{x}_t)\dot{x}_\beta(t) + \xi_\alpha(\mathbf{x}_t, t)$

Bogoliubov, 1945; Magalinskii, 1959; Zwanzig, 1973:

– Renormalized force: $\tilde{f}_\alpha(\mathbf{x}) = f_\alpha(\mathbf{x}) + F_\alpha\left(\mathbf{x},\overline{\mathbf{X}}_0\right) + \dfrac{\partial F_\alpha\left(\mathbf{x},\overline{\mathbf{X}}_0\right)}{\partial X_\mu}\overline{u}_\mu(\mathbf{x})$

where $\overline{u}_\mu(\mathbf{x}) = \dfrac{\left\langle u_\mu u_\nu \right\rangle_0}{k_B T} G_\nu(\mathbf{x},\overline{\mathbf{X}}_0)$

– Thermal noise:

$$\xi_\alpha(\mathbf{x},t) = \frac{\partial F_\alpha\left(\mathbf{x},\overline{\mathbf{X}}_0\right)}{\partial X_\mu} u_\mu(t) \;, \qquad \left\langle u_\mu(0) u_\nu(t) \right\rangle_0 \cong 2\delta(t)\int_0^\infty ds \left\langle u_\mu(0) u_\nu(s) \right\rangle_0$$

– Dissipation matrix:

$$\eta_{\alpha\beta}(\mathbf{x}) = \frac{\partial F_\alpha(\mathbf{x}_t,\overline{\mathbf{X}}_0)}{\partial X_\mu} \frac{\partial F_\beta(\mathbf{x}_s,\overline{\mathbf{X}}_0)}{\partial X_\nu} \int_0^\infty ds \frac{\left\langle u_\mu(0) u_\nu(s) \right\rangle_0}{k_B T}$$

New recipe

- Initial microscopic equations:

$$\dot{p}_\alpha = f_\alpha(\mathbf{x}) + F_\alpha(\mathbf{x},\mathbf{X}); \qquad \dot{P}_\mu = g_\mu(\mathbf{X}) + G_\mu(\mathbf{x},\mathbf{X})$$

- Langevin equation: $\dot{p}_\alpha = \tilde{f}_\alpha(\mathbf{x}) - \eta_{\alpha\beta}(\mathbf{x}_t)\dot{x}_\beta(t) + \xi_\alpha(\mathbf{x}_t, t)$

M.E. and P.Reimann, Phys. Rev. B **82**, 224303 (2010):

- Renormalized force: $\tilde{f}_\alpha(\mathbf{x}) = f_\alpha(\mathbf{x}) + F_\alpha\left(\mathbf{x}, \overline{\mathbf{X}}_0 + \overline{\mathbf{u}}(\mathbf{x})\right)$

  where $$\overline{u}_\mu(\mathbf{x}) = \frac{\langle u_\mu u_\nu \rangle_0}{k_B T} G_\nu(\mathbf{x}, \overline{\mathbf{X}}_0)$$

- Thermal noise:

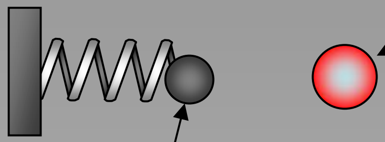
$$\xi_\alpha(\mathbf{x},t) = \frac{\partial F_\alpha\left(\mathbf{x}, \overline{\mathbf{X}}_0 + \overline{\mathbf{u}}(\mathbf{x},t)\right)}{\partial X_\mu} u_\mu(t) \;, \qquad \langle u_\mu(0) u_\nu(t) \rangle_0 \cong 2\delta(t) \int_0^\infty ds \langle u_\mu(0) u_\nu(s) \rangle_0$$

- Dissipation matrix:

$$\eta_{\alpha\beta}(\mathbf{x}) = \frac{\partial F_\alpha(\mathbf{x}_t, \overline{\mathbf{X}}_0 + \overline{\mathbf{u}}(\mathbf{x}))}{\partial X_\mu} \frac{\partial F_\beta(\mathbf{x}_s, \overline{\mathbf{X}}_0 + \overline{\mathbf{u}}(\mathbf{x}))}{\partial X_\nu} \int_0^\infty ds \frac{\langle u_\mu(0) u_\nu(s) \rangle_0}{k_B T}$$

Numerical test #1

- Model:



$$m\ddot{x} = -W'(x-X)$$

$$W(x) = \varepsilon\left((\sigma/x)^{12} - 2(\sigma/x)^{6}\right)$$

$$M\ddot{X} = -\kappa X + W'(x-X) - \gamma\dot{X} + \Xi(t)$$

$$\overline{X}_0 = 0\ ;\ \left\langle u^2 \right\rangle_0 = \frac{k_B T}{\kappa}\ ;\ \int_0^\infty dt \left\langle u(0)u(t) \right\rangle_0 = \frac{\gamma k_B T}{\kappa^2}$$

- Langevin equation: $m\ddot{x} = \tilde{f}(x) - \eta(x)\dot{x} + \xi(x,t)$

$$\tilde{f}(x) = -W'\left(x - \overline{u}(x)\right) \qquad \eta(x) = \gamma\left(\frac{W''\left(x - \overline{u}(x)\right)}{\kappa}\right)^2$$

$$\overline{u}(x) = W'(x)/\kappa$$

- Parameters: $\varepsilon = 4\, pN\, nm;\ \sigma = 0.5\, nm$

$m = 200\, yg;\ M = 100\, yg$

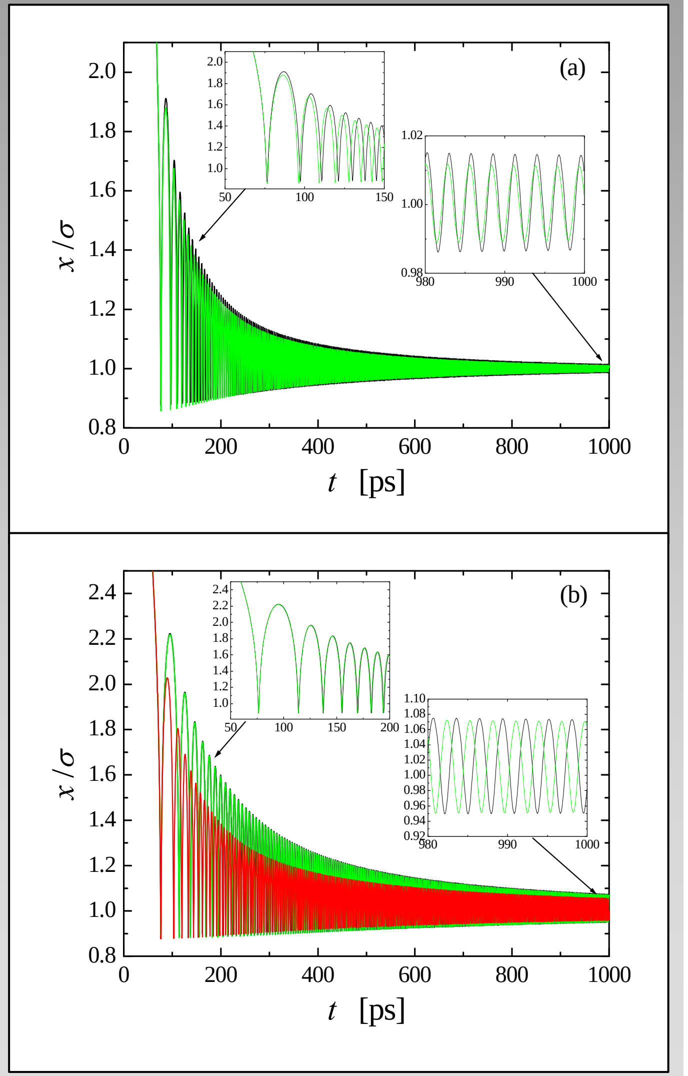
$X(0) = 0;\ \dot{X}(0) = 0$

$x(0) = 4\sigma;\ \dot{x}(0) = -10\, m/s$

$T = 0$

(a) $\kappa = 10 W''(\sigma)$

(b) $\kappa = 20 W''(\sigma)$

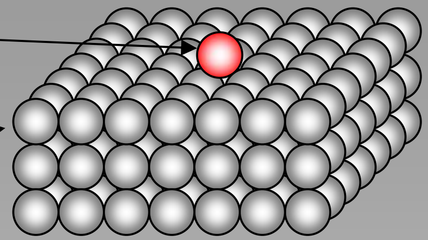


Numerical test #2

- Equations of motion:

$$m\ddot{\mathbf{r}} = -\sum_i \nabla W(\mathbf{r}-\mathbf{R}_i)$$

$$M\ddot{\mathbf{R}}_i = -\kappa(\mathbf{R}_i - \mathbf{R}_i^0) + \nabla W(\mathbf{r}-\mathbf{R}_i) - \gamma\dot{\mathbf{R}}_i + \mathbf{\Xi}_i(\mathbf{R}_i, t)$$



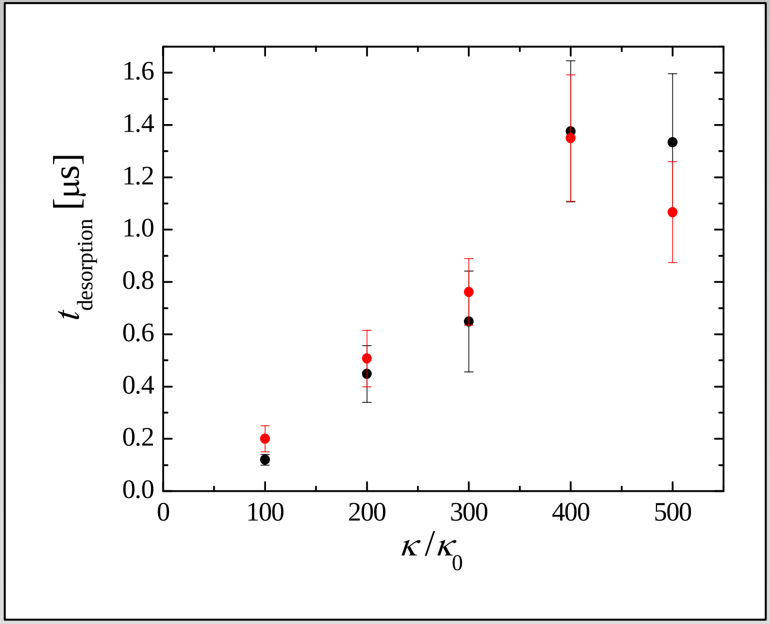
- Langevin equation: $m\ddot{r}_\alpha = \tilde{f}_\alpha(\mathbf{r}) - \eta_{\alpha\beta}(\mathbf{r})\,\dot{r}_\beta + \xi_\alpha(\mathbf{r},t)$

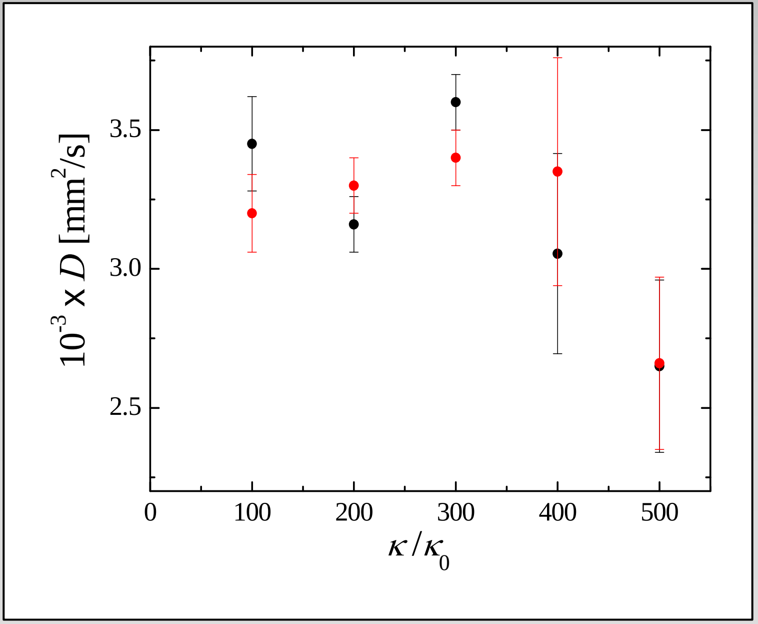
- Parameters:

$$W(\mathbf{r}) = \varepsilon\left((\sigma/r)^{12} - 2(\sigma/r)^6\right) \qquad m = 200\,\mathrm{yg};\ M = 100\,\mathrm{yg}$$

$$\varepsilon = 5\,\mathrm{pN\,nm};\ k_B T = 2\,\mathrm{pN\,nm} \qquad \gamma = \sqrt{\kappa M}\,/10$$

$$\sigma = a = 0.4\,\mathrm{nm} \qquad \kappa_0 = 72\,\varepsilon/\sigma^2$$





Conclusions

- Langevin equation can save you a great deal of computational effort

- Langevin equation is an approximation valid for
  - weak system-bath coupling
  - large time-scale separation between the (slow) system and (fast) bath degrees of freedom

- The new recipe for deriving Langevin equation improves its accuracy and increases its validity range by about an order of magnitude with respect to the system-bath coupling strength

- More details in

  M.E. and P.Reimann, Phys. Rev. B **82**, 224303 (2010)

- Acknowledgements

Deutsche Forschungsgemeinschaft (SFB 613) and
ESF programs NATRIBO and FANAS (project Nanoparma)