Langevin equation for a system nonlinearly coupled to a heat bath

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Motivation

- Molecular dynamics:

  \[ \mu \alpha \beta \gamma + \alpha \beta \gamma \alpha \gamma \alpha = \mu \gamma \alpha \beta \alpha \beta \]

- Stochastic dynamics:

  \[ \alpha \beta \gamma \alpha \beta \gamma \alpha = \mu \gamma \alpha \beta \alpha \beta \]

10\(^N\) atoms of the heat bath,
\(N < 10\)

\(n\) atoms of the system,
\(n \sim 1\ldots 10\)

Equations of motion:

System: \(\dot{P}_\alpha = f_\alpha (x) + F_\alpha (x, X)\)

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

Langevin equations of motion:

\(\dot{P}_\alpha = \tilde{f}_\alpha (x) - \eta_{\alpha\beta} (x) \dot{x}_\beta + \xi_\alpha (x_t, t)\)

Forces:
- renormalized
- dissipative
- random
Langevin simulation

• Langevin equation
  \[ \dot{p}_\alpha = \tilde{f}_\alpha (x_t) - \eta_{\alpha \beta} (x_t) \dot{x}_\beta (t) + \xi_{\alpha} (x_t, t) \]

• Noise
  – Unbiased: \[ \langle \xi_{\alpha} (x_t, t) \rangle = 0 \]
  – Gaussian and white: \[ \langle \xi_{\alpha} (x_t, t) \xi_{\beta} (x_s, s) \rangle = 2k_B T \eta_{\alpha \beta} (x_t) \delta(t - s) \]

• Implementation:
  \[ m_\alpha \frac{v_{\alpha}^{[n+1/2]} - v_{\alpha}^{[n-1/2]}}{\Delta t} = \tilde{f}_\alpha (x^{[n]}) - \eta_{\alpha \beta} (x^{[n-1]}) v_{\beta}^{[n-1/2]} + r_{\alpha}^{[n]} \]
  \[ x_{\alpha}^{[n+1]} = x_{\alpha}^{[n]} + v_{\alpha}^{[n+1/2]} \Delta t \]

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

\[ \langle r_{\alpha}^{[n]} \rangle = 0 ; \quad \langle r_{\alpha}^{[n]} r_{\beta}^{[k]} \rangle = 2k_B T \eta_{\alpha \beta} (x^{[n]}) \delta_{nk} / \Delta t \]
Plan of the derivation

- **Step 1.** From the heat bath equations of motion
  \[ \dot{P}_\mu = g_\mu(X) + G_\mu(x, X) \]
  approximately evaluate
  \[ X_\mu(t) \approx \bar{X}_\mu([x(t'<t)]) + u_\mu(t) \]
  (systematic part + noise)

- **Step 2.** Plug the result back into the system’s equations of motion:
  \[ \dot{p}_\alpha = f_\alpha(x) + F_\alpha(x, X) \approx f_\alpha(x) + F_\alpha(x, \bar{X}([x]) + u(t)) \]

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

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

- **Initial microscopic equations:**
  \[
  \dot{p}_\alpha = f_\alpha(x) + F_\alpha(x, X); \quad \dot{P}_\mu = g_\mu(X) + G_\mu(x, X)
  \]

- **Langevin equation:**
  \[
  \dot{p}_\alpha = \tilde{f}_\alpha(x) - \eta_{\alpha\beta}(x) \dot{x}_\beta(t) + \xi_\alpha(x, t)
  \]

  Bogoliubov, 1945; Magalinskii, 1959; Zwanzig, 1973:
  
  - **Renormalized force:**
    \[
    \tilde{f}_\alpha(x) = f_\alpha(x) + F_\alpha(x, \overline{X}_0) + \frac{\partial F_\alpha(x, \overline{X}_0)}{\partial X_\mu} \bar{u}_\mu(x)
    \]
    where
    \[
    \bar{u}_\mu(x) = \frac{\langle u_\mu u_\nu \rangle_0}{k_B T} G_\nu(x, \overline{X}_0)
    \]
  
  - **Thermal noise:**
    \[
    \xi_\alpha(x, t) = \frac{\partial F_\alpha(x, \overline{X}_0)}{\partial X_\mu} u_\mu(t), \quad \langle u_\mu(0) u_\nu(t) \rangle_0 \approx 2 \delta(t) \int_0^\infty ds \langle u_\mu(0) u_\nu(s) \rangle_0
    \]
  
  - **Dissipation matrix:**
    \[
    \eta_{\alpha\beta}(x) = \frac{\partial F_\alpha(x, \overline{X}_0)}{\partial X_\mu} \frac{\partial F_\beta(x, \overline{X}_0)}{\partial X_\nu} \int_0^\infty ds \frac{\langle u_\mu(0) u_\nu(s) \rangle_0}{k_B T}
    \]
• Initial microscopic equations:

\[ \dot{p}_\alpha = f_\alpha (x) + F_\alpha (x, X); \quad \dot{P}_\mu = g_\mu (X) + G_\mu (x, X) \]

• Langevin equation:

\[ \dot{p}_\alpha = \widetilde{f}_\alpha (x) - \eta_{\alpha\beta}(x_t)\dot{x}_\beta (t) + \xi_\alpha (x_t, t) \]


– Renormalized force:

\[ \widetilde{f}_\alpha (x) = f_\alpha (x) + F_\alpha (x, \overline{X}_0 + \overline{u}(x)) \]

where

\[ \overline{u}_\mu (x) = \frac{\langle u_\mu u_v \rangle_0}{k_BT} G_v (x, \overline{X}_0) \]

– Thermal noise:

\[ \xi_\alpha (x, t) = \frac{\partial F_\alpha (x, \overline{X}_0 + \overline{u}(x, t))}{\partial x_\mu} u_\mu (t), \quad \langle u_\mu (0)u_v (t) \rangle_0 \approx 2\delta(t) \int_0^\infty ds \langle u_\mu (0)u_v (s) \rangle_0 \]

– Dissipation matrix:

\[ \eta_{\alpha\beta}(x) = \frac{\partial F_\alpha (x_1, \overline{X}_0 + \overline{u}(x))}{\partial x_\mu} \frac{\partial F_\beta (x_0, \overline{X}_0 + \overline{u}(x))}{\partial x_\nu} \int_0^\infty ds \frac{\langle u_\mu (0)u_v (s) \rangle_0}{k_BT} \]
Numerical test #1

- **Model:**
  \[ m\ddot{x} = -W'(x - X) \]
  \[ W(x) = \varepsilon \left( (\sigma / x)^{12} - 2(\sigma / x)^6 \right) \]
  \[ M\ddot{X} = -\kappa X + W'(x - X) - \gamma \dot{X} + \Xi(t) \]

- **Langevin equation:**
  \[ m\ddot{x} = \tilde{f}(x) - \eta(x)\dot{x} + \xi(x,t) \]
  \[ \tilde{f}(x) = -W'(x - \bar{u}(x)) \]
  \[ \eta(x) = \gamma \left( \frac{W''(x - \bar{u}(x))}{\kappa} \right)^2 \]
  \[ \bar{u}(x) = W'(x) / \kappa \]

- **Parameters:**
  \[ \varepsilon = 4 \text{ pN nm}; \quad \sigma = 0.5 \text{ nm} \]
  \[ m = 200 \text{ yg}; \quad M = 100 \text{ yg} \]
  \[ X(0) = 0; \quad \dot{X}(0) = 0 \]
  \[ x(0) = 4\sigma; \quad \dot{x}(0) = -10 \text{ m/s} \]
  \[ T = 0 \]
• 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:

\[ W(\mathbf{r}) = \varepsilon \left( (\sigma/\mathbf{r})^{12} - 2(\sigma/\mathbf{r})^6 \right) \]

\[ m = 200 \text{ yg}; \quad M = 100 \text{ yg} \]

\[ \varepsilon = 5 \text{ pN nm}; \quad k_B T = 2 \text{ pN nm} \]

\[ \sigma = a = 0.4 \text{ nm} \]

\[ \gamma = \sqrt{\kappa M / 10} \]

\[ \kappa_0 = 72 \varepsilon / \sigma^2 \]
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

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