Approximation of quantum observables by molecular dynamics simulations

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Molecular dynamics

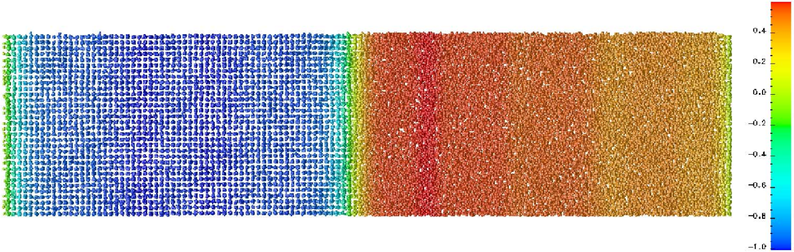

Figure: solid-liquid phase transition, von Schwerin & Szepessy (2010)

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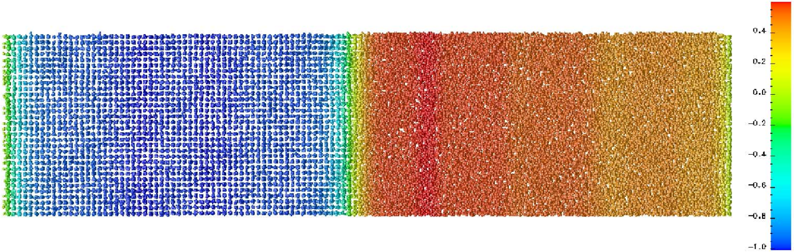

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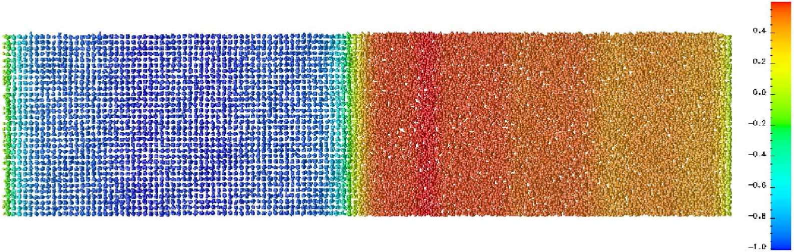

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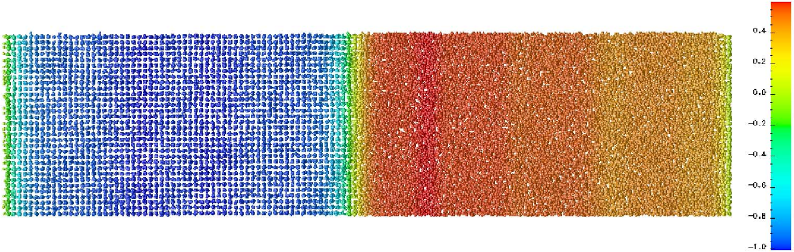

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The Schrödinger equation

Eigenvalue problem for the wavefunction and energy:

$$\hat{H}\Phi = E\Phi,$$

where the Schrödinger operator is

$$\hat{H} = -\sum_{k=1}^{M} \frac{1}{2M^k}\Delta_{X^k} - \sum_{i=1}^{N} \frac{1}{2}\Delta_{x^i} - \sum_{i=1}^{N}\sum_{k=1}^{M} \frac{z^k}{|x^i - X^k|} + \sum_{1\le i<j\le N} \frac{1}{|x^i - x^j|} + \sum_{1\le k<l\le M} \frac{z^k z^l}{|X^k - X^l|}$$

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The BO molecular dynamics is

$$M\ddot{X}_t = -\nabla\lambda_0(X_t)$$

Quantum canonical ensemble observables

$$\hat{H} = -\frac{1}{2M}\Delta + V(X),$$

with a matrix valued potential $V : \mathbb{R}^N \to \mathbb{C}^{d\times d}$.

Schrödinger: $\hat{H}\Phi_n = E_n\Phi_n$

Goal: determine $G := \sum_n \langle \Phi_n, \hat{A}\Phi_n\rangle e^{-E_n/T} / \sum_n e^{-E_n/T}$ for an observable $A : \mathbb{R}^{2N} \to \mathbb{C}^{d\times d}$ and temperature T.

Weyl quantization

$$\hat{A}\phi(x) = \int_{\mathbb{R}^N} \underbrace{\Big(\frac{M^{1/2}}{2\pi}\Big)^N \int_{\mathbb{R}^N} e^{iM^{1/2}(x-y)\cdot p} A\big(\frac{x+y}{2}, p\big)\, dp}_{L^2\text{-kernel}}\ \phi(y) dy$$

so $\widehat{V(x)} = V(x)$, $\frac{\widehat{|p|^2}}{2} = -\frac{1}{2M}\Delta$ and thus $H(x,p) = \frac{|p|^2}{2} + V(x)$.

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$$\begin{aligned}\sum_n \langle \Phi_n, \hat{A}\Phi_n\rangle &= \text{trace } \hat{A}\\ &= \text{trace } (L^2\text{-kernel})\\ &= \Big(\frac{M^{1/2}}{2\pi}\Big)^N \int_{\mathbb{R}^{2N}} \text{trace } A(x,p)dxdp\end{aligned}$$

In fact also

$$\sum_n \langle \Phi_n, \hat{A}\hat{B}\Phi_n \rangle = \Big(\frac{M^{1/2}}{2\pi}\Big)^N \int_{\mathbb{R}^{2N}} \text{trace } \big(A(z)B(z)\big)\, dz.$$

We choose $B = e^{-H/T}$ and assume

$$H(z) = \Psi(x)\tilde{H}(z)\Psi^*(x), \quad \text{where } \tilde{H}_{jk}(z) = \delta_{jk}\Big(\frac{|p|^2}{2} + \lambda_j(x)\Big),$$
$$A(z) = \Psi(x)\tilde{A}(z)\Psi^*(x), \quad \text{where } \tilde{A}(z) \text{ diagonal}$$

and $V(x) = \Psi(x)\Lambda(x)\Psi^*(x)$.

Connection quantum - classical

Thus

$$\frac{\sum_n \langle \Phi_n, \hat{A}\widehat{e^{-H/T}}\Phi_n\rangle}{\sum_n \langle \Phi_n, \widehat{e^{-H/T}}\Phi_n\rangle} = \frac{\sum_{j=1}^{d} \int_{\mathbb{R}^{2N}} \tilde{A}_{jj}(z) e^{-\tilde{H}_{jj}(z)/T}\, dz}{\sum_{j=1}^{d} \int_{\mathbb{R}^{2N}} e^{-\tilde{H}_{jj}(z)/T}\, dz}$$

For the LHS we use
Lemma

$$G = \frac{\sum_n \langle \Phi_n, \hat{A}\Phi_n\rangle e^{-E_n/T}}{\sum_n e^{-E_n/T}} = \frac{\sum_n \langle \Phi_n, \hat{A}e^{-\hat{H}/T}\Phi_n\rangle}{\sum_n \langle \Phi_n, e^{-\hat{H}/T}\Phi_n}$$

$$= \frac{\sum_n \langle \Phi_n, \hat{A}\widehat{e^{-H/T}}\Phi_n\rangle}{\sum_n \langle \Phi_n, \widehat{e^{-H/T}}\Phi_n\rangle} + \mathcal{O}(M^{-1/2})$$

We rewrite the RHS:

$$\frac{\sum_n \langle \Phi_n, \hat{A}\widehat{e^{-H/T}}\Phi_n\rangle}{\sum_n \langle \Phi_n, \widehat{e^{-H/T}}\Phi_n\rangle} = \frac{\sum_{j=1}^d \int_{\mathbb{R}^{2N}} \tilde{A}_{jj}(z) e^{-\tilde{H}_{jj}(z)/T}\, dz}{\sum_{j=1}^d \int_{\mathbb{R}^{2N}} e^{-\tilde{H}_{jj}(z)/T}\, dz}$$

$$= \sum_{j=1}^d q_j \int_{\mathbb{R}^{2N}} \tilde{A}_{jj}(z) \frac{e^{-\tilde{H}_{jj}(z)/T}\, dz}{\int_{\mathbb{R}^{2N}} e^{-\tilde{H}_{jj}(z')/T}\, dz'} =: \sum_{j=1}^d q_j A_j$$

based on the probabilities

$$q_j := \frac{\int_{\mathbb{R}^{2N}} e^{-\tilde{H}_{jj}(z)/T}\, dz}{\sum_{k=1}^d \int_{\mathbb{R}^{2N}} e^{-\tilde{H}_{kk}(z')/T}\, dz'}, \quad j = 1, \ldots, d$$

to be in state j.

$$A_j := \int_{\mathbb{R}^{2N}} \tilde{A}_{jj}(z) \frac{e^{-\tilde{H}_{jj}(z)/T}}{\int_{\mathbb{R}^{2N}} e^{-\tilde{H}_{jj}(z')/T}\, dz'}\, dz$$

is by ergodicity

$$A_j = \lim_{\tau\to\infty} \tau^{-1} \int_0^\tau \tilde{A}_{jj}(Z_t)\, dt\,,$$

where $Z_t = (X_t, P_t)$ solves the Langevin equation

$$\begin{aligned} dX_t &= P_t\, dt \\ dP_t &= -\nabla\lambda_j(X_t)\, dt - \alpha P_t\, dt + \sqrt{2\alpha T}\, dW_t\,. \end{aligned} \tag{2}$$

Similarly the probabilities q_j can be computed using molecular dynamics.

Theorem linking quantum and MD

$$G := \frac{\sum_n \langle \Phi_n, \hat{A}\Phi_n \rangle e^{-E_n/T}}{\sum_n e^{-E_n/T}} = \lim_{\tau\to\infty} \sum_{k=1}^{d} q_k \int_0^\tau \tilde{A}_{kk}(Z_t^k) \frac{dt}{\tau} + \mathcal{O}(M^{-1/2}),$$

where

$$\begin{aligned} Z_t^k &= (X_t, P_t) \text{ with } \lambda_k, \\ q_k &= \frac{\bar{q}_k}{\sum_{i=1}^d \bar{q}_i}, \\ \bar{q}_k &= \lim_{\tau\to\infty} \int_0^\tau e^{-\frac{\lambda_k(X_t^1) - \lambda_1(X_t^1)}{T}} \frac{dt}{\tau}. \end{aligned}$$