Corrections to Molecular Simulations: Fundamentals and Practice

By Saman Alavi

Chapter 2

Page 11

$$\begin{aligned}E(t) &= K(t)+U(t) = mv_{\xi}(t)^2/2 + k\xi(t)^2/2 \\ &= \left[m\omega^2 A^2 \cos^2(\omega t+\phi) + kA^2 \sin^2(\omega t+\phi)\right]/2 = kA^2\end{aligned} \tag{2.13}$$

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The one-dimensional motion of a mass subject to the Lennard-Jones potential placed at five initial ~~placements of the mass at~~ positions near $r^*(0) = r(0)/\sigma = 1$, with initial momentum of $p^*(0) = 0$ are shown in Figure 1.4(b).

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For the object moving perpendicular to the surface of the earth under the operation of a velocity-dependent atmospheric drag force, Newton's second law is,

$$m\frac{d^2y}{dt^2} = F_y = mg - bv_y = mg - b\frac{dy}{dt}. \tag{2.18}$$

$$\left(\frac{d^2y}{dt^2} + \frac{b}{m}\frac{dy}{dt}\right)e^{bt/m} = \frac{d}{dt}\left(e^{bt/m}\frac{dy}{dt}\right) = ge^{bt/m}. \tag{2.19}$$

$$v_y(t) = v_y(0)e^{-bt/m} + \frac{mg}{b}\left(1-e^{-bt/m}\right). \tag{2.20}$$

At long times, the velocity approaches the so-called the terminal velocity $+mg/b$.

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$$y(t) = y(0) + \left[v_y(0) - \frac{mg}{b}\right]\frac{m}{b}\left(e^{-bt/m} - 1\right) + \frac{mg}{b}t \tag{2.21}$$

$$m\frac{d^2y}{dt^2}v_y - mgv_y = -bv_y^2, \tag{2.22}$$

$$\frac{d}{dt}\left[\frac{1}{2}m\left(\frac{dy}{dt}\right)^2 - mgy\right] = -bv_y^2\,. \tag{2.23}$$

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Using diagrams introduced by Michael P. Allen and Dominic J. Tildesley, the flow of Euler's method is shown schematically in Figure 2.6.

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In the leap-frog algorithm, the Taylor expansion of the velocity, Eq.(2.27) is written for half time

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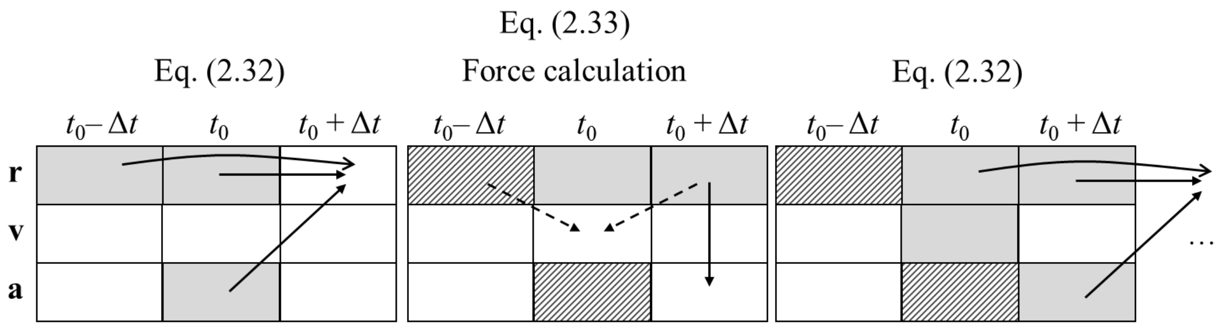

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If the positions (and thus forces) and velocities are known as some time t_0, the Euler relations for the motion of the N-atom system are,

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This connection is explored in Chapter 6 after concepts of statistical mechanics are introduced.

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The Lagrangian is written in terms of coordinates, $\mathbf{q}$, and ~~their~~ conjugate velocities, $\dot{\mathbf{q}}$ of the particles in the system.

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$$L=\frac{1}{2}m\dot{\xi}^2-\frac{1}{2}k\xi^2 \qquad (2.44)$$

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$$p_i=\frac{\partial L}{\partial \dot{\xi}_i}=m\dot{\xi}\,, \qquad (2.49)$$

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$$\begin{cases}\mathbf{R}_{cm}=\dfrac{m_1\mathbf{r}_1+m_2\mathbf{r}_2}{m_1+m_2}\\ \mathbf{r}_{rel}=\mathbf{r}_{12}=\mathbf{r}_2-\mathbf{r}_1\end{cases} \qquad (2.A.2)$$

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Determining the second derivatives of $\mathbf{R}_{cm}$ and $\mathbf{r}_{rel}$ from Eq. (2.A.3) and using Eq.(2.A.1) gives two new equations of motion for the center of mass and relative motion,

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$$\begin{cases}\dfrac{d^2\mathbf{R}_{cm}}{dt^2}=0\\ \dfrac{d^2\mathbf{r}_{rel}}{dt^2}=\dfrac{m_1+m_2}{m_1m_2}F_{12}\left(\mathbf{r}_{rel}\right)=\dfrac{1}{\mu}F_{12}\left(\mathbf{r}_{rel}\right)\end{cases} \qquad (2.A.4)$$

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In the new coordinate system, the motion of the center of mass and relative coordinates are not coupled.

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The Lagrangian equations of motion Eq. (2.43) for this system become

Chapter 3

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In classical ~~mechanical~~ molecular dynamics or Monte Carlo simulations, this assumption is still used, but provisions are made so that the forces incorporate aspects of quantum mechanical behaviour which are needed to accurately model the system.

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$$\left[\sum_{k=1}^{N_{nuc}}\frac{-\hbar^2}{2m_{nuc,k}}\hat{\nabla}_k^2+\sum_{j=1}^{N_{ele}}\frac{-\hbar^2}{2m_e}\hat{\nabla}_j^2+\frac{1}{4\pi\varepsilon_0}\left(\sum_{k,\ell=1}^{N_{nuc}}\frac{Q_kQ_\ell}{\left|\mathbf{R}_k-\mathbf{R}_\ell\right|}+\sum_{i,j=1}^{N_{ele}}\frac{q_iq_j}{\left|\mathbf{r}_i-\mathbf{r}_j\right|}+\sum_{k=1}^{N_{nuc}}\sum_{j=1}^{N_{ele}}\frac{q_jQ_k}{\left|\mathbf{r}_j-\mathbf{R}_k\right|}\right)\right]\psi_n(\{\mathbf{r},\mathbf{R}\})$$
$$=E_n\psi_n(\{\mathbf{r},\mathbf{R}\})\qquad(3.12)$$

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A crucial approximation, which provides the justification for introducing the familiar classical ball-and-spring type of intramolecular potentials between atoms in classical molecular simulations~~,~~ is the Born-Oppenheimer approximation named after the physicists Max Born and J. Robert Oppenheimer (1927).

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This mass ratio is close to that of the mass of a typical bowling ball (~6 kg) to a ping-pong ball (~3 g) which is ~2000. An electron and nuclei interact with the same Coulombic force ~~and gain the same acceleration~~ from their interaction but the mass of the electrons is so much smaller that they will move much faster in molecules than the nuclei.

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$$\hat{H}_{ele}=\sum_{j=1}^{N_{ele}}\left[\frac{-\hbar^2}{2m_e}\hat{\nabla}_j^2+\frac{1}{4\pi\varepsilon_0}\left(\sum_{k=1}^{N_{nuc}}\frac{q_jQ_k}{\left|\mathbf{r}_j-\mathbf{R}_k\right|}+\sum_{i=1}^{N_{ele}}\frac{q_iq_j}{\left|\mathbf{r}_i-\mathbf{r}_j\right|}\right)\right].\qquad(3.A.2)$$

Chapter 4

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$$\mathbf{h}=\begin{pmatrix} L_{a,x} & L_{b,x} & L_{c,x} \\ L_{a,y} & L_{b,y} & L_{c,y} \\ L_{a,z} & L_{b,z} & L_{c,z} \end{pmatrix}. \tag{4.1}$$

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$$\phi_i(r_i)=\frac{1}{4\pi\varepsilon_0}\sum_{\mathbf{n}}{}'\left(\sum_{j=1}^{N}\frac{q_j}{|\mathbf{r}_{ij}+\mathbf{n}|}\right). \tag{4.13}$$

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$$g(k_x)=g(0)e^{-k_x^2\sigma^2/2}=\frac{1}{\sqrt{2\pi}}e^{-k_x^2\sigma^2/2}=\frac{1}{\sqrt{2\pi}}e^{-k_x^2/2\sigma_k^2}. \tag{4.A.5}$$

The value of $g(0)=1/\sqrt{2\pi}$ is determined from Eq.(4.A.2) and the normalization condition of the Gaussian function.

Chapter 5

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$$\frac{dP(v_x)}{dv_x}\frac{1}{P(v_x)v_x} = C' \Rightarrow \frac{dP(v_x)}{P(v_x)} = C'v_x dv_x \Rightarrow \ln P(v_x) = -Cv_x^2 + B\,, \tag{5.41}$$

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This is an example of importance sampling where random numbers sampling the “importance function” *F*(*x*), can be mapped back onto the *x*-values to generate the ~~onto~~ probability distribution *f*(*x*).

Chapter 6

Page 143

Figure 6.1. The seven possible distributions ~~(microstates)~~ of five molecules among available one-molecule quantum states in a hypothetical system with a total energy $E_{\text{tot}} = 5\Delta$.

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The values of the degeneracy of each distribution~~microstate~~ are given in Table 6.1.

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By adding two additional molecules to the system, the numbers of possible distributions and corresponding microstates have increased substantially from 7 to 15, and from 216 to 1716, respectively.

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The probability for this distribution~~microstate~~ is significantly greater than many of the other distributions~~microstates~~ in this macrostate.

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For macroscopic systems with molecules of the the order of 10^{23} or so, the most probable distribution has such a overwhelmingly larger probability that the contributions of other distributions~~microstates~~ can effectively be neglected in determining system properties.

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There can be many distributions~~*microstates*~~ with N molecules distributed among the quantum states ε_i such that the total system macrostate has an energy E_N.

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Any distribution of the ensemble~~system~~ among the states must satisfy the conditions,

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$$\Lambda\left(\{A_i\};\alpha,\beta\right)=\mathcal{A}\ln\mathcal{A}-\sum_j A_j\ln A_j-\alpha\left(\sum_j A_j-\mathcal{A}\right)-\beta\left(\sum_j A_jE_j-\mathcal{E}\right) \tag{6.21}$$

Both A_j in the first sum should have j as subscript.

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… and the macroscopic energy of the system in the ensemble effectively becomes …

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$$\begin{aligned}\Delta(N,P,T)&=\sum_{V_\ell}e^{-PV_\ell/kT}\sum_j e^{-E_j(V_\ell,N)/kT}\\&=\sum_{V_\ell}e^{-PV_\ell/kT}\sum_E\Omega(N,V_\ell,E)e^{-E(V_\ell,N)/kT}\\&=\sum_{V_\ell}Q(N,V_\ell,E)e^{-PV_\ell/kT}\end{aligned}$$

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It is more convenient to express the thermodynamic variables in the isothermal-isobaric ensemble in terms of $\ln\Delta(N,T,P)$.

$$\begin{aligned}\langle H(N,T,P)\rangle&=\sum_{V_\ell}\sum_i P_i(V_\ell)\left[E_i(V_\ell,N)-PV_\ell\right]=kT^2\left[\frac{\partial\ln\Delta(N,T,P)}{\partial T}\right]\\&=\frac{\sum_{V_\ell}e^{-PV_\ell/kT}\sum_i\left[E_i(V_\ell,N)-PV_\ell\right]e^{-E_i(V_\ell,N)/kT}}{\sum_{V_k}e^{-PV_k/kT}\sum_j e^{-E_j(V_k,N)/kT}}\end{aligned}$$

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$$\sum_j e^{-E_j/kT} \to \frac{1}{N!h^{3N}} \int \cdots \int e^{-\mathcal{H}(\{\mathbf{p},\mathbf{q}\})/kT} d\mathbf{p}_1 d\mathbf{q}_1 \cdots d\mathbf{p}_N d\mathbf{q}_N \,, \tag{6.93}$$

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$$\omega(\varepsilon + \Delta\varepsilon) = \phi(\varepsilon + \Delta\varepsilon) - \phi(\varepsilon) = \frac{d\phi(\varepsilon)}{d\varepsilon} \Delta\varepsilon = 2\pi \left(\frac{2m}{h^2} \right)^{3/2} V \varepsilon^{1/2} \Delta\varepsilon \,. \tag{6.A.7}$$

Chapter 7

Page 179

Upon a system volume change, after first scaling the molecule center of mass positions in fractional coordinates, they are transformed back to Cartesian coordinates and then the new internal atomic positions are determined~~s are positioned~~ with respect to the new center of mass position according to Eq. (7.1).

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"…velocity-dependent drag force in friction and hydrodynamics with p_η/W playing the role of a time-dependent drag constant, see Sec. 2.3~~2~~.4."

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This value is used in Eq. (7.26) and allows the calculation of a second estimate $\mathbf{v}^{(2)}(t)$ (fourth line of Eq. (7.26)), which can be reused to get the second estimate $\mathrm{T}^{(2)}(t)$.

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To compare the behavior of the system temperature under the operation of the Nose-Hoover and Berendsen thermostats, consider simulations performed on a system of 8000 atoms interacting with a Lennard-Jones potential discussed by Ber~~e~~k Hess.

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The action of the Nosé-Hoover thermostat with a reduced oscillation period of $t^* = (t/\sigma)\sqrt{(\varepsilon/m)} = 1$ and a Berendsen thermostat with scaling time constant of $\tau_T'^* = 0.5$ are shown in Fig. 6.5.

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This shows that average kinetic energy per molecule and therefore the temperature associated with the average energy show finite fluctuations for the ideal gas and this also holds in the canonical ensemble. Isokinetic methods which scale the average kinetic energy per molecule to exactly correspond to the desired external temperature will not give a canonical ensemble distribution function. Equation (7.28) can be used to determine the expression for the fluctuations in temperature. Using the definition of temperature associated with the average kinetic energy per molecule, $T_K = (1/N)\sum_{i=1}^{N} mv_i^2/3k$, we determine,

$$\begin{aligned} T_K^2 &= \frac{1}{N^2}\sum_{i=1}^{N} mv_i^2/3k\sum_{j=1}^{N} mv_j^2/3k \\ &= \frac{1}{N^2}\left[N\sum_{i=1}^{N} m^2v_i^4/9k^2 + N(N-1)\sum_{i=1}^{N} mv_i^2/3k\sum_{j\neq i}^{N} mv_j^2/3k\right] \\ &= \frac{4}{9k^2N}\left\langle \varepsilon_K^2\right\rangle + \frac{4(N-1)}{9k^2N}\left\langle \varepsilon_K\right\rangle\left\langle \varepsilon_K\right\rangle \end{aligned} \tag{7.29}$$

In the limit of very large systems, the fluctuations in temperature go to zero, but in simulations of finite systems, even "constant temperature" molecular dynamics simulations show temperature fluctuations when measured by the average molecular kinetic energy.

A simple approach to applying a thermostat and barostat together may seem to be the simultaneous combination of the Andersen barostat and Nosé thermostat Hamiltonians for a system as given in Eqs. (7.11~~5~~) and (7.25~~23~~).

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These six values are used in Eq. (7.36) and allow the calculation of a second estimate $\mathbf{v}^{(2)}(t)$ and $\mathbf{r}^{(2)}(t+\Delta t/2)$ (sixth and seventh lines of Eq. (7.36)), which can be reused to get the second set of estimates $\mathrm{T}^{(2)}(t)$, $\mathrm{P}^{(2)}(t)$, $\zeta^{(2)}(t)$, and $\eta^{(2)}(t)$.

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$$s_0 = \exp\left[\frac{-\left(\mathcal{H}_0(\mathbf{p},\mathbf{r}) + p_s^2/2Q - E\right)}{N_f kT_{ext}}\right] \tag{A.7.9}$$

Chapter 8

Page 208

$$\left\langle dN(r)\right\rangle = \frac{1}{N_t}\sum_{t_k=1}^{N_t}\left\langle dN(r,t_k)\right\rangle . \tag{8.4}$$

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$$g(\mathbf{r}_1,\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2 = g(r)d\mathbf{r}_1 d\mathbf{r} = g(r)d\mathbf{r}_1 r^2 dr \sin\theta d\theta d\phi , \tag{8.38}$$

$$\frac{dN(r)}{N} = \int_V \int_0^{\pi}\int_0^{2\pi}\frac{1}{N^2}g(r)d\mathbf{r}_1 \sin\theta d\theta d\phi r^2 dr = \frac{V}{N^2}g(r)4\pi r^2 dr \tag{8.39}$$

Chapter 9

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At short times the displacement has time dependence similar to a mass moving under a constant (gravitational) force given in Eq. (2.4) of Sec. 2.~~2~~3.1 and is called the “ballistic motion regime”.

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In a gas sample, collisions with other molecules in the gas change the orientation of the molecule and dampen the rotational motion and therefore lead to the decay of the amplitude of the oscillations in ~~$u(t)\cdot u(0)$~~ $\mathbf{u}(t)\cdot\mathbf{u}(0)$ (see Figure 9.10(a)).

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“As discussed Sec. 2.~~2~~3.4, the operation of a drag force causes the velocity of a mass to decay …”

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“In the short time limit, $e^{-\zeta t} \rightarrow 1 - \zeta t$ and …”

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$$D = \frac{1}{3}\int_0^{\infty} \langle \mathbf{v}(0)\cdot\mathbf{v}(t)\rangle\, dt \qquad (9.A.35)$$

Chapter 10

Page 260

“…, which allows calculation of average values of macroscopic mechanical and thermodynamic variables.”

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$$\begin{aligned} x_{new,j} &= x_{old,j} + \eta_1 \times 2\Delta r_{max} \\ y_{new,j} &= y_{old,j} + \eta_2 \times 2\Delta r_{max} \\ z_{new,j} &= z_{old,j} + \eta_3 \times 2\Delta r_{max} \end{aligned} \qquad (10.6)$$

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“Gas adsorption can be studied more efficiently using the grand canonical Monte Carlo (GCMC) simulation technique …”

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“~~(X)~~ $\langle X \rangle$ is the (as of yet unknown) average value of collective property X and σ_X is the standard deviation of the distribution of the average. The $\langle X \rangle$~~(X)~~ can be considered …”

$$\begin{aligned} \sigma_X^2 &= \left\langle \left(X - \langle X \rangle \right)^2 \right\rangle = \frac{1}{N^2} \left\langle \left[x_1 + x_2 + \ldots + x_N - \langle x_1 + x_2 + \ldots + x_N \rangle \right]^2 \right\rangle \\ &= \frac{1}{N^2} \sum_{i=1}^{N} \sigma_x^2 = \frac{1}{N} \sigma_x^2 \end{aligned}$$

This is a special application of the central limit theorem for the collective variable X defined in Eq. (10.43), which is the average of the individual stochastic variables x_i.

To clarify this analysis, consider an example suggested by Sachin Shanbhag [271].