Computational Rheology via LAMMPS, October 12, 2013
85th Meeting of the Society of Rheology

7: Common Equilibrium Calculations

Jeremy B. Lechman
Engineering Sciences Center
Sandia National Laboratories,
Albuquerque, New Mexico

Sandia National Laboratories is a multi program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Observables and Ensemble Averages

- Variables in MD/particle-based simulation
  - $\mathbf{r}(t) = (\mathbf{r}_1(t), \mathbf{r}_2(t), \ldots, \mathbf{r}_N(t))$; $\mathbf{p}(t) = (\mathbf{p}_1(t), \mathbf{p}_2(t), \ldots, \mathbf{p}_N(t))$
  - What we really are interested in is some (macroscopic) observable, $O = O(\mathbf{r}(t),\mathbf{p}(t))$
  - How to obtain?
    - Ensemble Average
      - Average over all possible values of $\mathbf{r}(t)$ and $\mathbf{p}(t)$; given $f^N(\mathbf{r},\mathbf{p})$
        - » Note: in equilibrium there is no time dependence of f^N

$$\overline{O}(\mathbf{r},\mathbf{p}) = \langle O \rangle_{ens} = \int\int O(\mathbf{r},\mathbf{p}) f^N(\mathbf{r},\mathbf{p})\, d\mathbf{r}\, d\mathbf{p}$$

    - In MD practice

$$\overline{O}(\mathbf{r},\mathbf{p},t_{obs}) = \langle O \rangle_{time} = \lim_{t_{obs}\to\infty} \frac{1}{t_{obs}} \int_0^{t_{obs}} O(\mathbf{r}(t),\mathbf{p}(t))\, dt$$

    - Note for Ergodic systems
      - Simulation big/long “enough”? $\langle O \rangle_{time} = \langle O \rangle_{ens}$

Thermodynamic Averages

- Calculated by LAMMPS `compute`(s)
  - Useful simulation diagnostic
- Temperature – `compute temp`
  - Equipartition of energy

$$\langle \mathcal{K} \rangle = \left\langle \sum_{i=1}^{N} p_i^2 / 2m_i \right\rangle = \frac{3}{2} N k_B T$$

  - Instantaneous kinetic temperature

$$\mathcal{T}(t) = \frac{1}{3Nk_B} \sum_{i=1}^{N} p_i^2(t) / m_i$$

    - Not the thermodynamic temperature

Thermodynamics Averages

- Pressure – `compute pressure`
  - Kinetic (ideal) part + potential (nonideal or excess) part

$$PV = Nk_B T + \langle \mathcal{W} \rangle$$

  - Virial equation

$$\mathcal{W} = \frac{1}{3}\sum_{i=1}^{N} \mathbf{r}_i \cdot \mathbf{f}_i$$

Evans and Morris, *Statistical Mechanics of Nonequilibrium Liquids*

  - Instantaneous

$$\mathcal{P}(t) = \rho k_B \mathcal{T}(t) + \mathcal{W}(t)/V$$

    - Not the thermodynamic pressure

- Pressure or Stress Tensor

$$\sigma_{\alpha\beta} = \left\langle \frac{1}{V}\sum_{i=1}^{N}\left[\sum_{j\neq i}\frac{r_{ij}^{\alpha} f_{ij}^{\beta}}{2} + m_i v_i^{\alpha} v_j^{\beta}\right]\right\rangle$$

Fluctuations

- Particle simulations give more than averages
  - Statistical information is available too!
    - Fluctuations and (spatial/temporal) Correlations
- Fluctuations in (macro) observables are of interest

$$\delta A_{obs} = A_{obs} - \langle A \rangle_{ens}$$

  - Example: fluctuations in thermodynamic quantities
    - Specific heats
    - Coefficient of thermal expansion
    - Isothermal compressibility

Thermodynamic Fluctuations

- Specific Heat via Thermodynamic Fluctuation Theory
  - See, e.g., Landau and Liftshitz (1980) *Statistical Physics*

$$\left\langle \delta E^2 \right\rangle = k_B T^2 C_V$$

  - In MD practice (e.g., Allen and Tildesley, *Computer Simulation of Liquids*)

$$\left\langle \delta E^2 \right\rangle = \left\langle \delta \mathcal{H}^2 \right\rangle_{NVT} = \left\langle \delta \mathcal{K}^2 \right\rangle_{NVT} + \left\langle \delta \mathcal{V}^2 \right\rangle_{NVT}$$

  - Recall from equipartition $\left\langle \delta \mathcal{K}^2 \right\rangle_{NVT} = \frac{3N}{2}\left(k_B T\right)^2$

$$\left\langle \delta \mathcal{V}^2 \right\rangle_{NVT} = k_B T^2 \left(C_V - \frac{3}{2} N k_B \right)$$

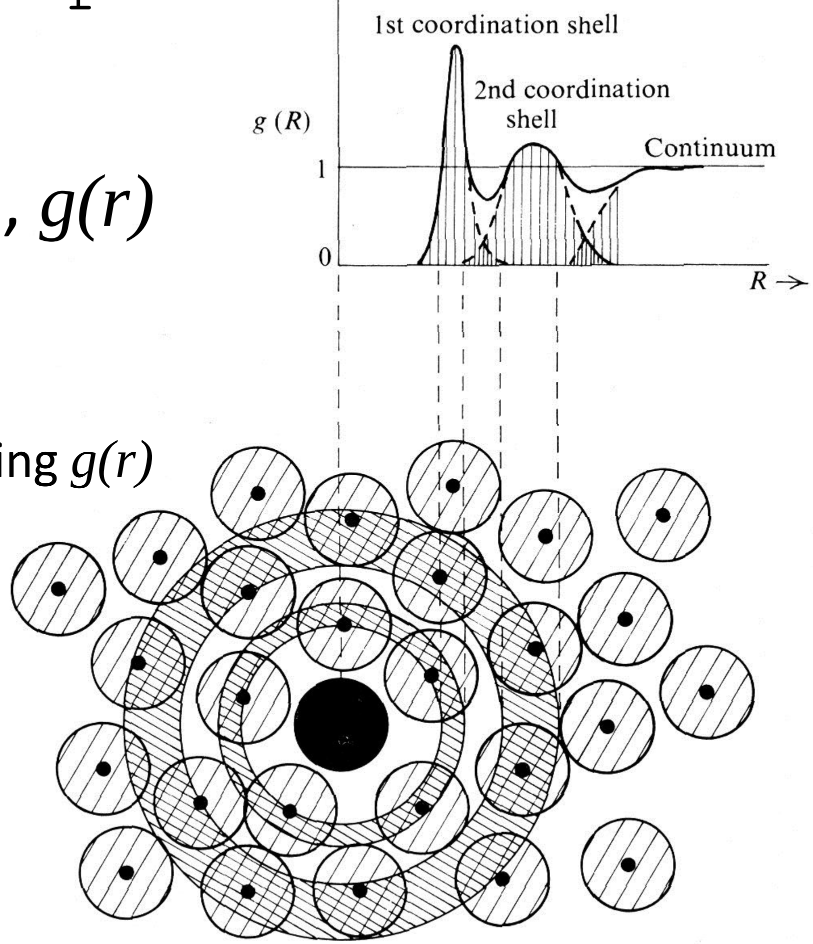
- Isothermal Compressibility $\left\langle \delta V^2 \right\rangle_{NPT} = V k_B T \beta_T$

Structural Quantities

- Correlation Functions – `compute rdf`
  - Pair correlation and Radial Distribution Function (RDF), *g(r)*
    - Usefulness
      - Ensemble average of any pair function may be expressed using *g(r)*
        - » Density, energy, pressure, chemical potential

$$\left\langle \frac{1}{N}\sum_{i}\sum_{j\neq i}\delta(r-r_j+r_i)\right\rangle = \rho g(r)$$

$$P = \rho k_B T + \frac{2\pi\rho^2}{3}\int \frac{dU(r)}{dr}\, g(r)\, r^3 dr$$



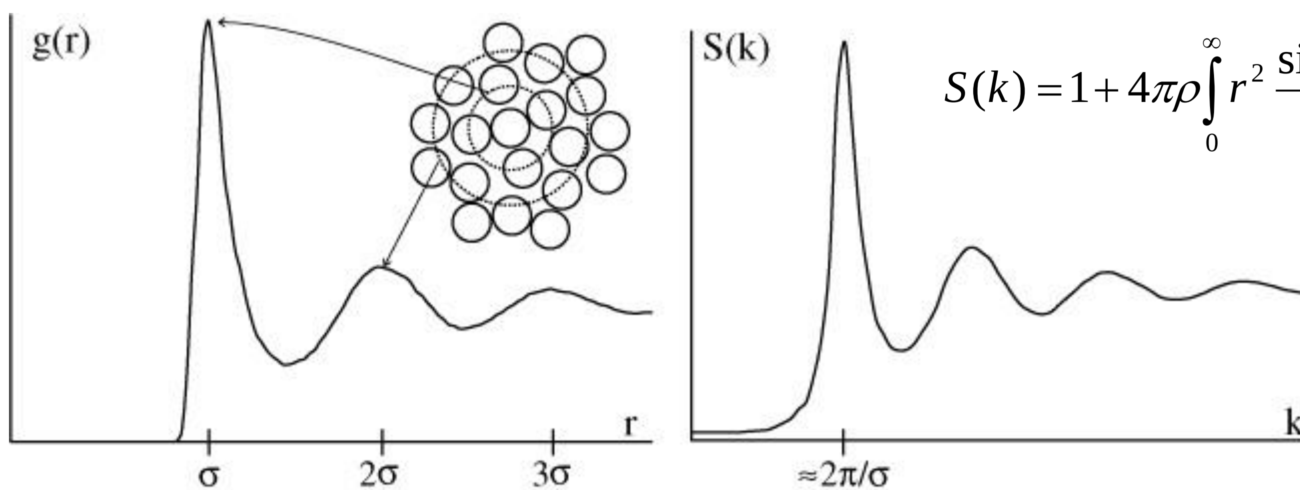
Typical fluid-like RDF

    - Measurable via radiation-scattering

Structural Quantities (cont.)

– Structure Factor

$$S(k) = N^{-1}\langle \rho(k)\rho(-k) \rangle \qquad \rho(k) = \sum_{i=1}^{N} \exp\left[i\mathbf{k}\cdot\mathbf{r}_i\right]$$



$$S(k) = 1 + 4\pi\rho \int_0^{\infty} r^2 \frac{\sin(kr)}{kr} g(r)\,dr$$

– Intermediate Scattering Function

$$I(k,t) = N^{-1}\langle \rho(k,t)\rho(-k,0) \rangle$$

- Van Hove function

Hansen and McDonald, *Theory of Simple Liquids*

Temporal Correlation Functions

- Relation to transport coefficients
  - Linear Response Theory (Green-Kubo)
    - Diffusion $$D = \frac{1}{3}\int_0^\infty \langle \mathbf{v}_i(t)\cdot\mathbf{v}_i(t')\rangle dt'$$
    - Shear Viscosity – `compute pxy`, `fix ave/correlate`

$$j_{\alpha\beta}(t) = \frac{1}{V}\sum_{i=1}^{N}\left[\sum_{j\neq i}\frac{r_{ij}^{\alpha}(t)\, f_{ij}^{\beta}(t)}{2} + m_i v_i^{\alpha}(t) v_j^{\beta}(t)\right]$$

$$\eta = \frac{V}{k_B T}\int_0^\infty \left\langle j_{\alpha\beta}(t)\cdot j_{\alpha\beta}(t')\right\rangle dt'$$

    - Bulk Viscosity
    - Thermal conductivity
- Others, e.g. orientation correlations, etc.
- Also useful in non-equilibrium settings

Zwanzig, R., *Nonequilibrium Statistical Mechanics*

Einstein Relations

- Diffusion – `compute msd`

$$2Dt = \frac{1}{3}\left\langle \left|\mathbf{r}_i(t) - \mathbf{r}_i(0)\right|^2 \right\rangle$$

Helfand, E. (1960), *Phys Rev*, v. 119, p. 1

- Viscosity

$$2\eta t = \frac{V}{k_B T}\left\langle \left(Q_{\alpha\beta}(t) - Q_{\alpha\beta}(0)\right)^2 \right\rangle$$

$$Q_{\alpha\beta} = \frac{1}{V}\sum_i r_i^{\alpha} p_i^{\beta}$$

  – See LAMMPS How to section 6.21 for various viscosity techniques