Lecture 11

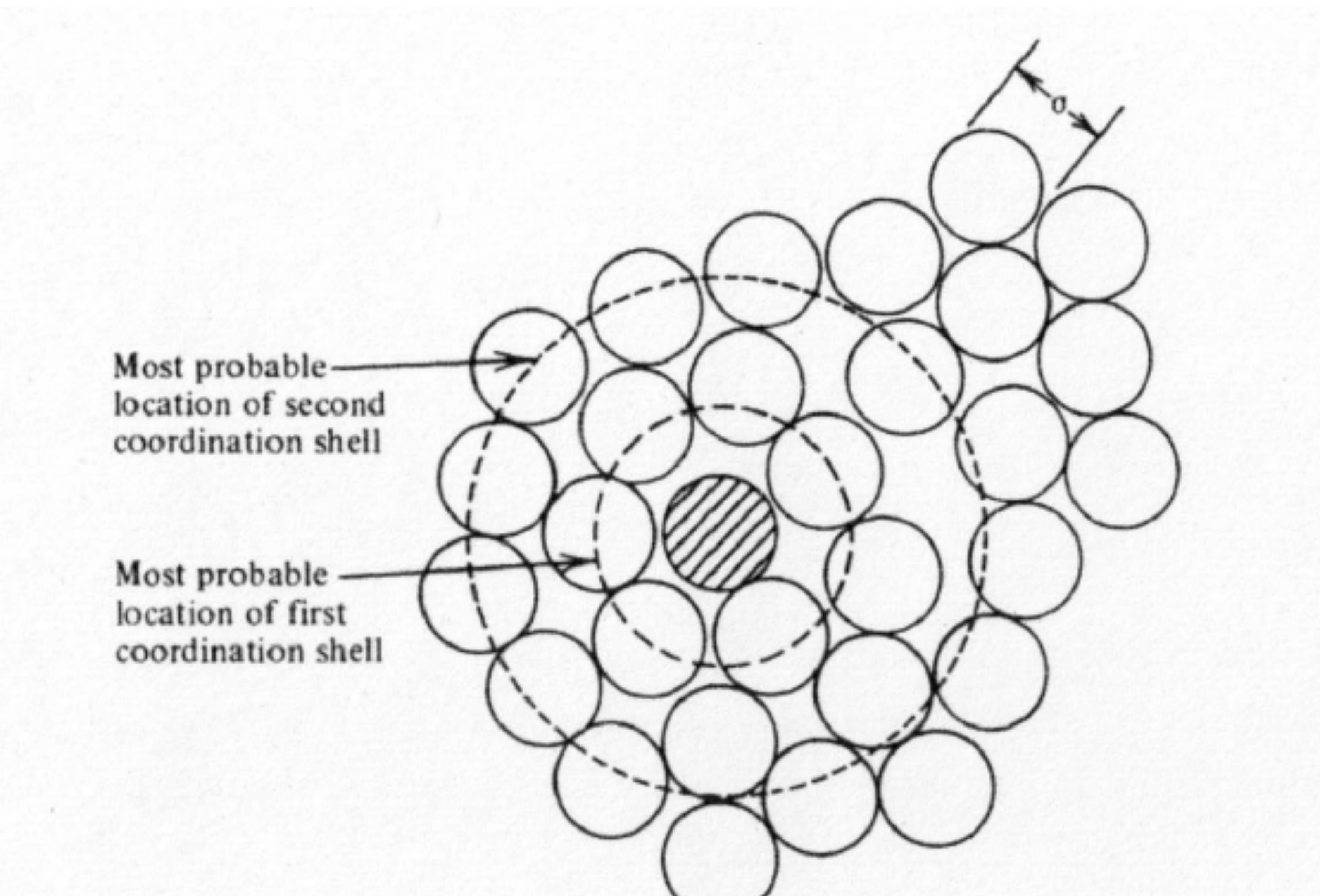
CHM695

Feb. 12

Radial Distribution Function

$$g(r) = \frac{(N-1)}{4\pi\rho r^2} \left\langle \delta(r - r') \right\rangle_{r',\theta',\phi',\mathbf{R}}$$

(also called pair distribution function)



It measures the probability of finding two particles at a distance r in NVT ensemble

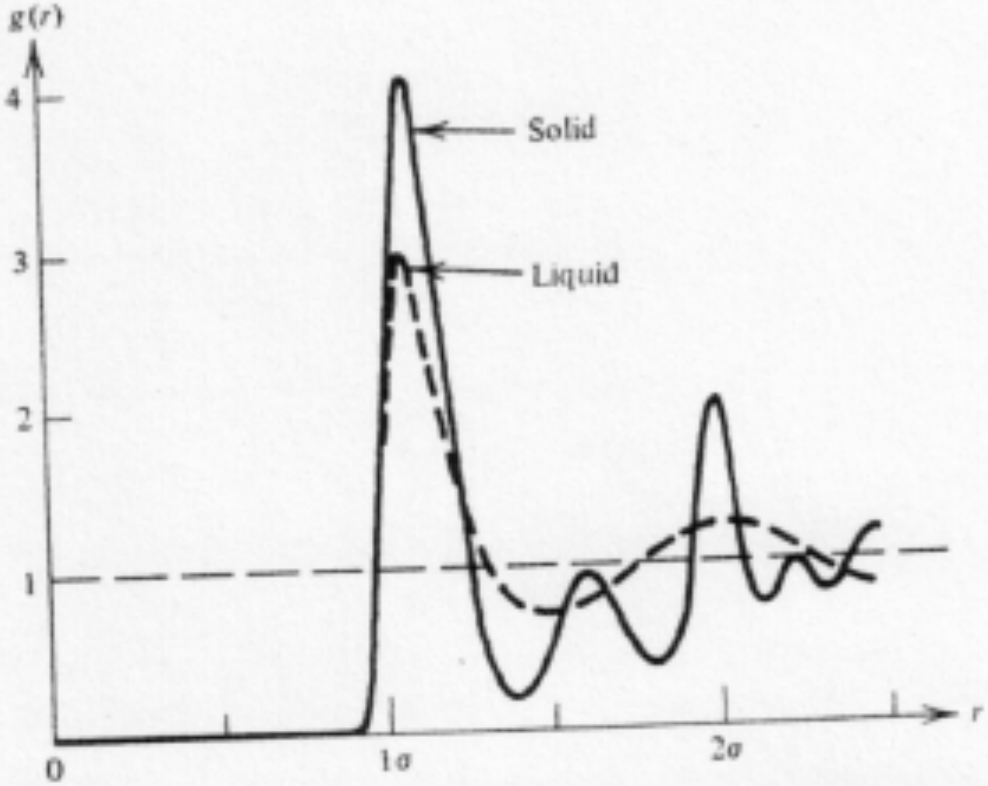
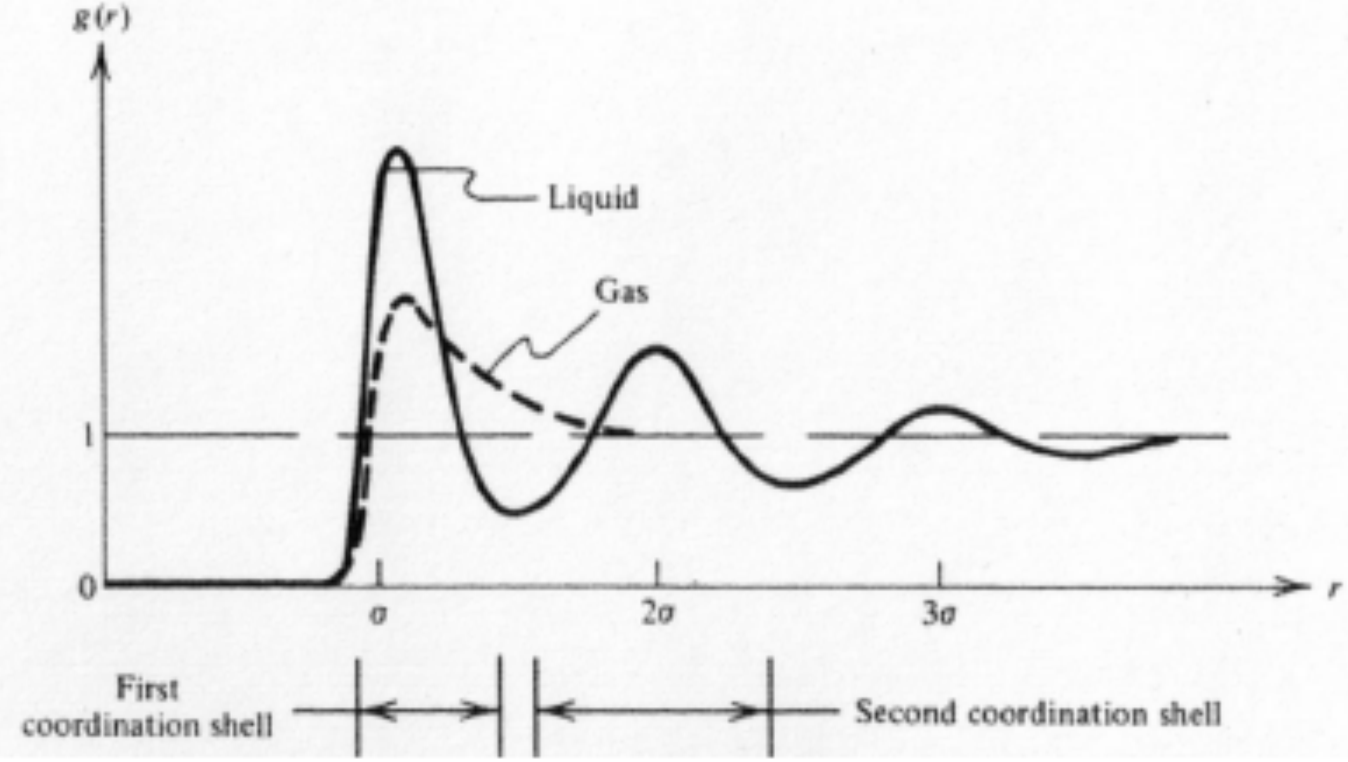


Fig. 7.5. Radial distribution functions for liquid and solid argon at the triple point ($\sigma = 3.4$ Å).



Coordination Number:

$$N_c = 4\pi\rho \int_0^{r_{\min}} r^2 g(r) dr$$

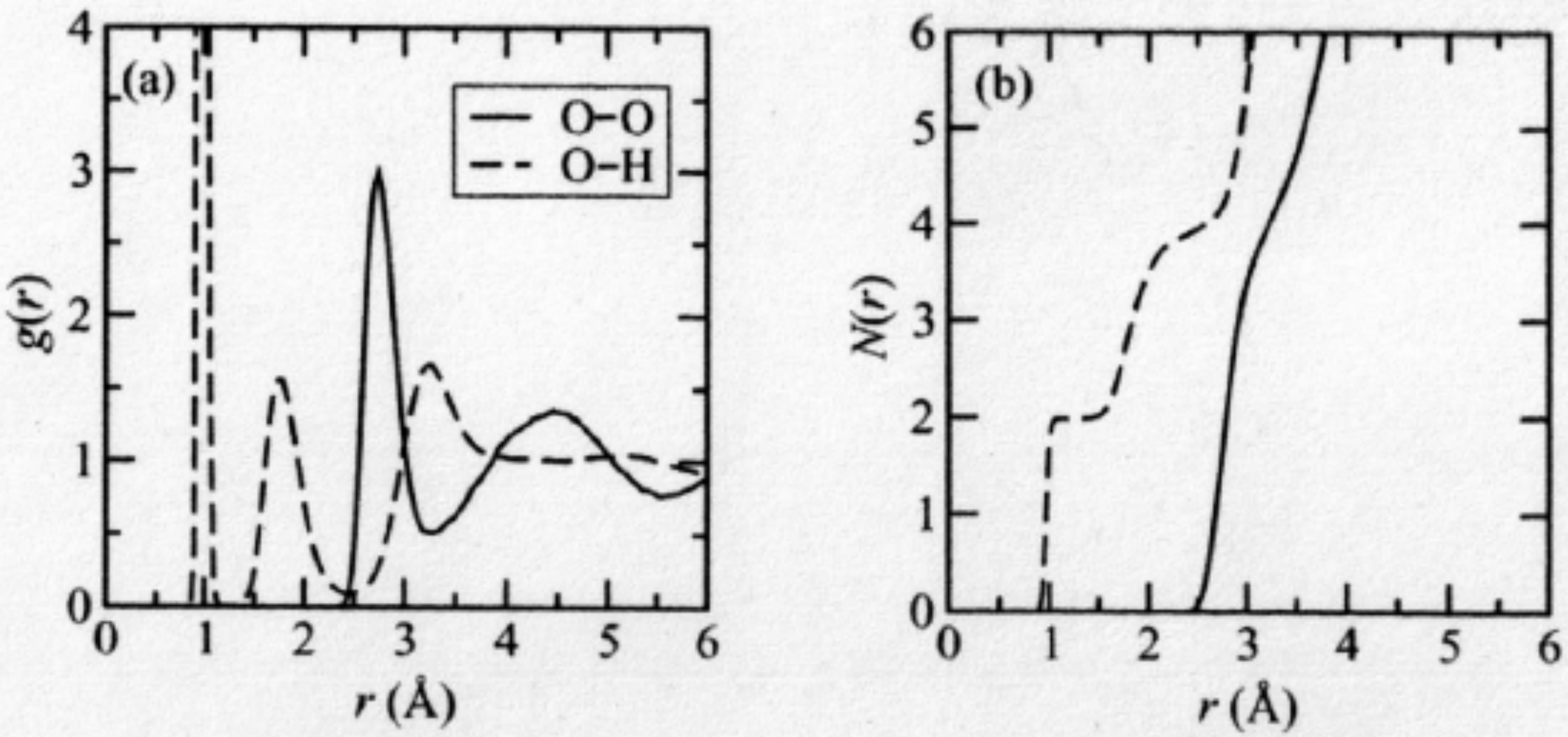
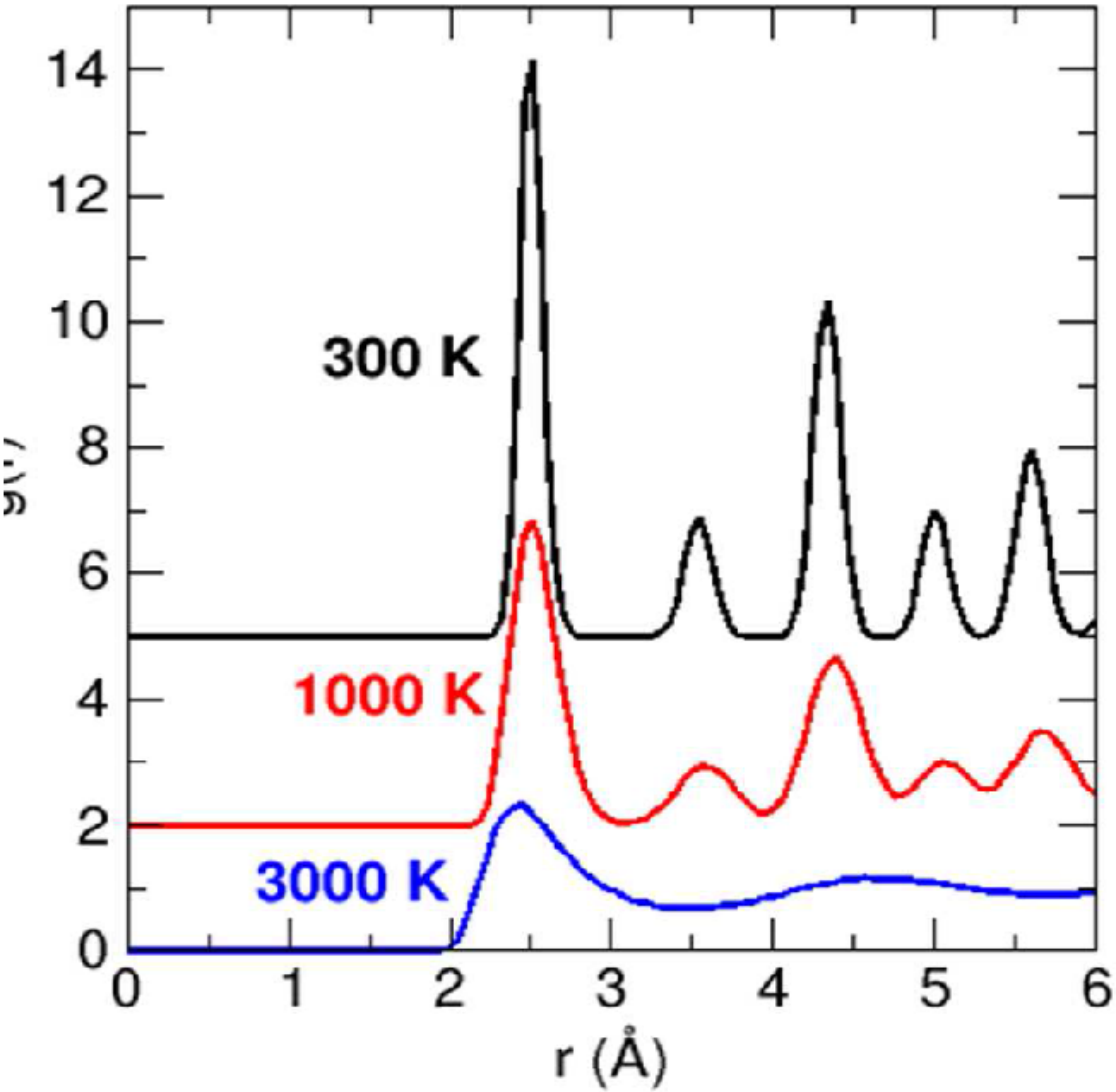
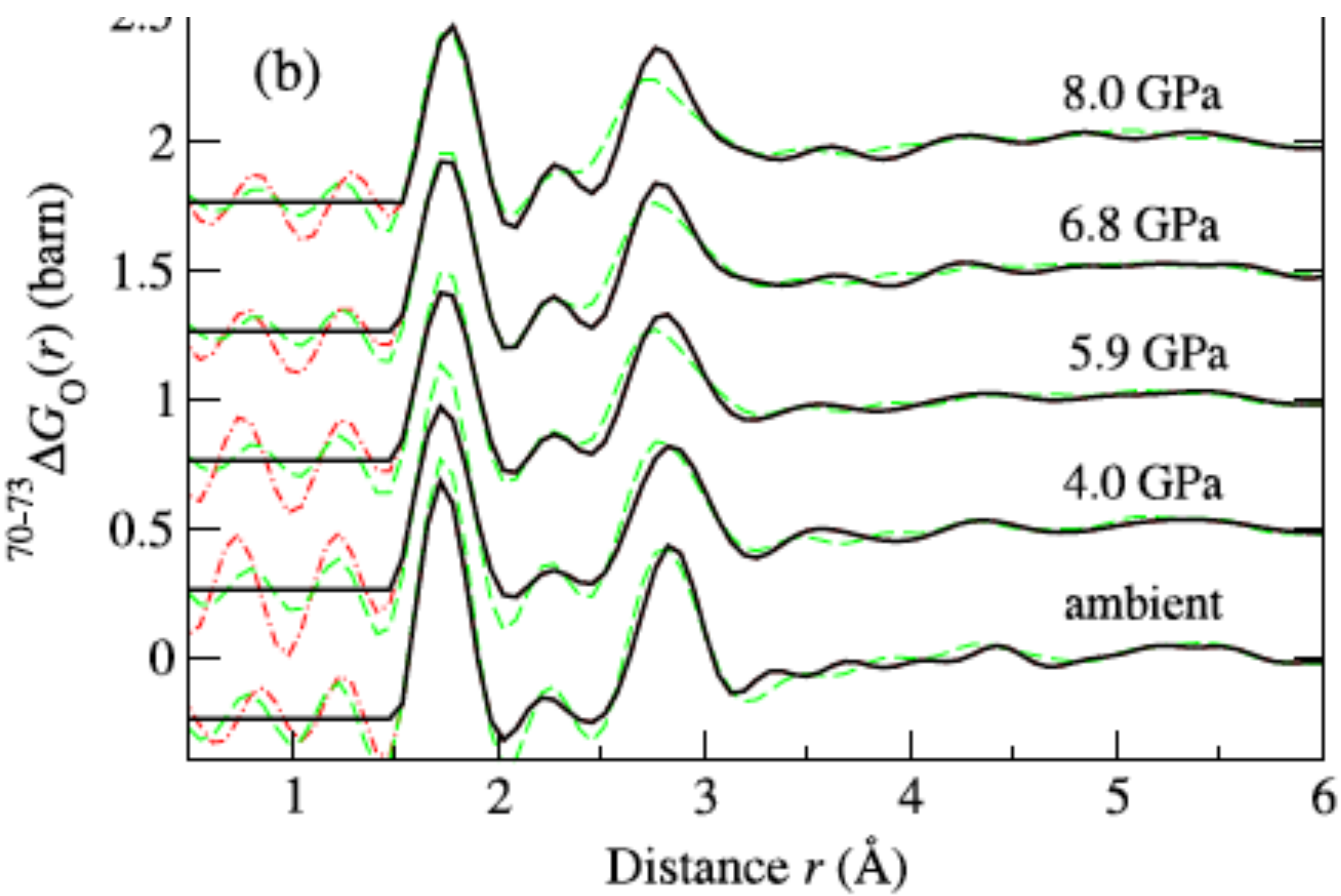


Fig. 4.3 (a) Oxygen–oxygen (O–O) and oxygen–hydrogen (O–H) radial distribution functions for a particular model of water (Lee and Tuckerman, 2006; Marx *et al.*, 2010). (b) The corresponding running coordination numbers computed from eqn. (4.6.23).

For a system at different temperatures, the following g(r) is obtained: interpret these results.



Pair distribution function can be also extracted from XRD
or
neutron scattering
(inverse Fourier transform)



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green: MD
red: X-ray

Structure Factor

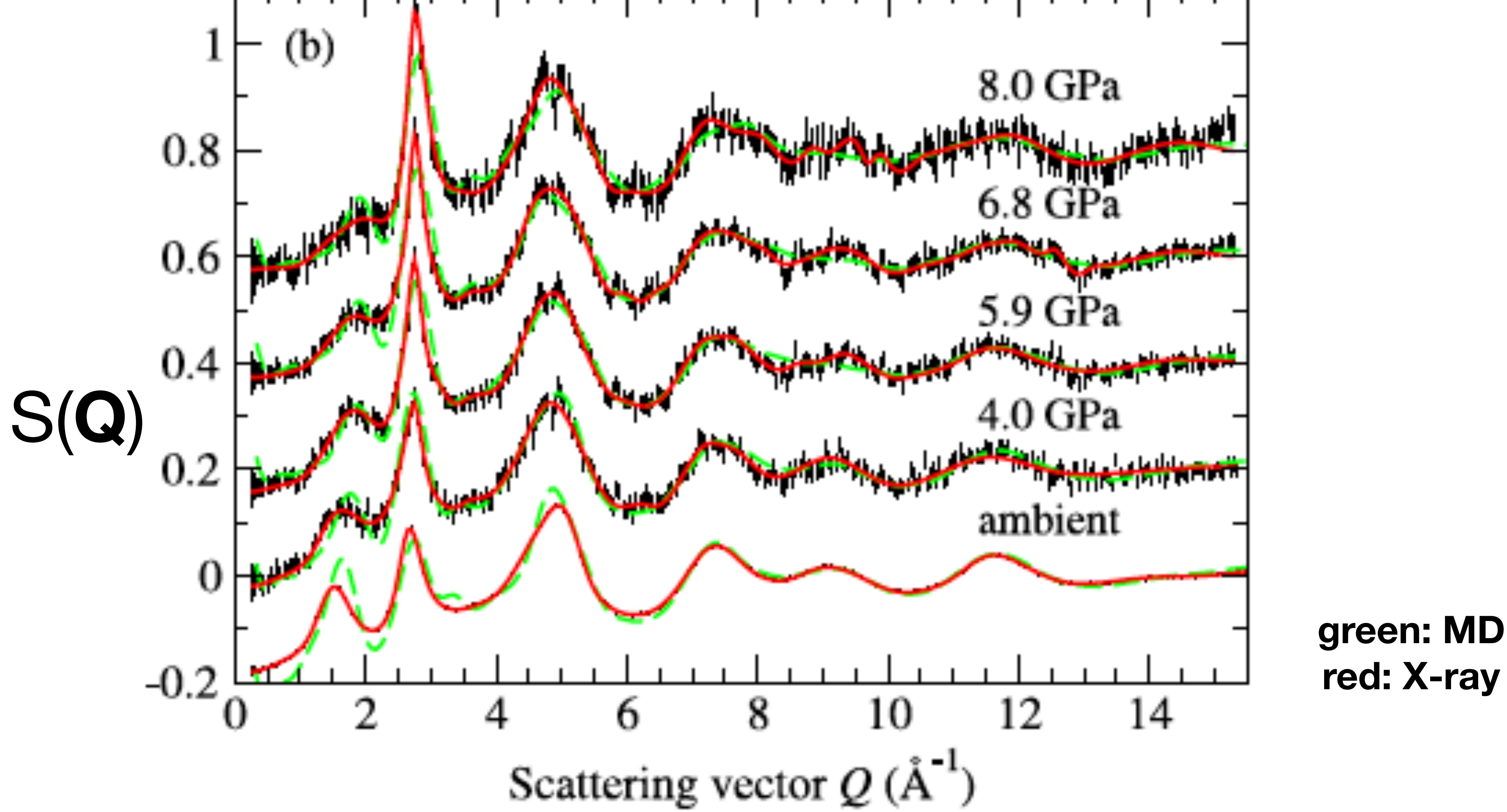
$$S(\mathbf{k}) = 1 + \frac{1}{N}\int d\mathbf{r}\int d\mathbf{r}'\exp\left(-i\mathbf{k}\cdot[\mathbf{r}-\mathbf{r}']\right)\rho\left(\mathbf{r},\mathbf{r}'\right)$$

$$\rho\left(\mathbf{r},\mathbf{r}'\right) = \left\langle \sum_{I}^{N}\sum_{J}^{N}\delta\left(\mathbf{r}-\mathbf{R}_I\right)\,\delta\left(\mathbf{r}'-\mathbf{R}_J\right)\right\rangle$$

For isotropic systems, this can be simplified to

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

sine transform of g(r)



oxygen

structural factors in GeO2 computed from $gO_O(r)$

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For algorithm of $g(r)$ see Frenkel & Smit

Advanced Techniques

Multiple Timestep Integrators

Classical evolution operators:

Consider a property $a(\mathbf{X})$ that can be evaluated as a function of time.

Using chain rule: $$\frac{da}{dt} = \sum_{\alpha=1}^{3N} \left[\frac{\partial a}{\partial q_\alpha} \dot{q}_\alpha + \frac{\partial a}{\partial p_\alpha} \dot{p}_\alpha \right]$$

We know that $\dot{q}_\alpha = \dfrac{\partial H}{\partial p_\alpha}$ and $\dot{p}_\alpha = -\dfrac{\partial H}{\partial q_\alpha}$

poisson bracket

Liouville operator

$$\frac{da}{dt} = \sum_{\alpha=1}^{3N} \left[\frac{\partial a}{\partial q_\alpha} \frac{\partial H}{\partial p_\alpha} - \frac{\partial a}{\partial p_\alpha} \frac{\partial H}{\partial q_\alpha} \right] = \{a, H\} = iLa$$

$$iL = \sum_{\alpha=1}^{3N} \left[\frac{\partial H}{\partial p_\alpha} \frac{\partial}{\partial q_\alpha} - \frac{\partial H}{\partial q_\alpha} \frac{\partial}{\partial p_\alpha} \right]$$

$$\frac{da}{dt} = iLa$$

has the formal solution:

$$a(\mathbf{X}_t) = \exp(iLt)a(\mathbf{X}_0)$$

$$iL_1 = \sum_{\alpha=1}^{3N} \frac{\partial H}{\partial p_\alpha} \frac{\partial}{\partial q_\alpha} \qquad iL_2 = -\sum_{\alpha=1}^{3N} \frac{\partial H}{\partial q_\alpha} \frac{\partial}{\partial p_\alpha}$$

$$iL = iL_1 + iL_2$$

$$iL_1\, iL_2\, f(\mathbf{X}) \neq iL_2\, iL_1\, f(\mathbf{X})$$

Trotter's Theorem

$$\exp(A+B) = \lim_{P\to\infty} \left[\exp(B/2P)\ \exp(A/P)\ \exp(B/2P)\right]^P$$

$$\begin{aligned}\exp(iLt) &= \exp(iL_1 t + iL_2 t)\\ &= \lim_{P\to\infty} \left[\exp(iL_2 t/2P)\ \exp(iL_1 t/P)\ \exp(iL_2 t/2P)\right]^P\end{aligned}$$

Let us define: $\Delta t = t/P$ **Then,** $P \to \infty \Rightarrow \Delta t \to 0$

For small Δt

$$\exp(iLt/P) \equiv \exp(iL\Delta t) \approx \left[\exp(iL_2\Delta t/2)\ \exp(iL_1\Delta t)\ \exp(iL_2\Delta t/2)\right]$$

$$e^{iL\Delta t}x(0) = x(\Delta t)$$

$$e^{iL\Delta t}p(0) = p(\Delta t)$$

$$e^{iL\Delta t} \approx \exp\left(\frac{\Delta t}{2}F(x)\frac{\partial}{\partial p}\right)\,\exp\left(\Delta t\frac{p}{m}\frac{\partial}{\partial x}\right)\exp\left(\frac{\Delta t}{2}F(x)\frac{\partial}{\partial p}\right)$$

$$\exp\left(c\frac{d}{dx}\right)g(x) = g(x+c)$$

First operator:

$$\exp\left(\frac{\Delta t}{2}F(x(0))\frac{\partial}{\partial p}\right)\begin{pmatrix} x(0) \\ \\ p(0) \end{pmatrix} = \begin{pmatrix} x(0) \\ \\ p(0) + \frac{\Delta t}{2}F(x(0)) \end{pmatrix}$$

Second operator:

$$\exp\left(\Delta t\frac{p(0)}{m}\frac{\partial}{\partial x}\right)\begin{pmatrix} x(0) \\ \\ p(0) + \frac{\Delta t}{2}F(x(0)) \end{pmatrix} = \begin{pmatrix} x(0) + \Delta t\frac{p(0)}{m} \\ \\ p(0) + \frac{\Delta t}{2}F\left(x(0) + \Delta t\frac{p(0)}{m}\right) \end{pmatrix}$$

Third operator:

$$\exp\left(\frac{\Delta t}{2}F(x(0))\frac{\partial}{\partial p}\right)\begin{pmatrix} x(0)+\frac{\Delta t}{m}p(0) \\ \\ p(0)+\frac{\Delta t}{2}F\left(x(0)+\Delta t\frac{p(0)}{m}\right) \end{pmatrix}$$

$$=\begin{pmatrix} \boxed{x(0)+\frac{\Delta t}{m}\left[p(0)+\frac{\Delta t}{2}F(x(0))\right]} \\ \boxed{p(0)+\frac{\Delta t}{2}F(x(0))+\frac{\Delta t}{2}F\left(x(0)+\frac{\Delta t}{m}\left[p(0)+\frac{\Delta t}{2}F(x(0))\right]\right)} \end{pmatrix}$$

$$
\begin{aligned}
x(\Delta t) &= x(0) + \frac{\Delta t}{m}\left[p(0) + \frac{\Delta t}{2}F(x(0))\right] \\
&= x(0) + v(0)\Delta t + \frac{\Delta t^2}{2m}F(x(0))
\end{aligned}
$$

$$
\begin{aligned}
p(\Delta t) &= p(0) + \frac{\Delta t}{2}F(x(0)) + \frac{\Delta t}{2}F\left(x(0) + \frac{\Delta t}{m}\left[p(0) + \frac{\Delta t}{2}F(x(0))\right]\right) \\
&= p(0) + \frac{\Delta t}{2}F(x(0)) + \frac{\Delta t}{2}F(x(\Delta t)) \\
v(\Delta t) &= v(0) + \frac{\Delta t}{2m}\left[F(x(0)) + F(x(\Delta t))\right]
\end{aligned}
$$

These are the velocity Verlet update of positions and velocities!

$$F(x) = F_{\text{fast}}(x) + F_{\text{slow}}(x)$$

$$iL = \frac{p}{m}\frac{\partial}{\partial x} + \left[F_{\text{fast}}(x) + F_{\text{slow}}(x)\right]\frac{\partial}{\partial p}$$

$$iL_{\text{fast}} = \frac{p}{m}\frac{\partial}{\partial x} + F_{\text{fast}}(x)\frac{\partial}{\partial p}$$

$$iL_{\text{slow}} = F_{\text{slow}}(x)\frac{\partial}{\partial p}$$

$$\exp(iL\Delta t) = \exp(iL_{\text{slow}}\Delta t/2)\,\boxed{\exp(iL_{\text{fast}}\Delta t)}\,\exp(iL_{\text{slow}}\Delta t/2)$$

factorise this time step to
smaller time steps

$$\exp(iL_{\text{fast}}\Delta t) = \left[\exp\left(\frac{\delta t}{2}F_{\text{fast}}\frac{\partial}{\partial p}\right)\exp\left(\delta t\frac{p}{m}\frac{\partial}{\partial x}\right)\exp\left(\frac{\delta t}{2}F_{\text{fast}}\frac{\partial}{\partial p}\right)\right]^n$$

Reference System Propagator Algorithm (RESPA)

Molecular dynamics algorithm for multiple time scales: Systems with long range forces

Mark E. Tuckerman[a] and Bruce J. Berne
Department of Chemistry, Columbia University, New York, New York 10027

Glenn J. Martyna
Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104

The Journal of Chemical Physics **94**, 6811 (1991);
https://doi.org/10.1063/1.460259

```
do j=1,n_outer

   call calculate_slow_force

   p=p+0.5*dt_large*F_slow

     do i=1,n
          p=p+0.5*dt_small*F_fast
          x=x+dt_small*p/m
          call calculate_fast_force
          p=p+0.5*dt_small*F_fast
      end do

   p=p+0.5*dt_large*F_slow
end do
```

Home work

1. For a harmonic oscillator

$$U(x,y) = \frac{1}{2}k_1 x^2 + \frac{1}{2}k_2 y^2$$

$$k_1 = 10\,k_2$$

a) integrate EOMs using one timestep (which is of course decided by k1)

b) integrate EOMs using multiple timesteps - note that k1 > k2, thus the force on x is fast and that on y is slow