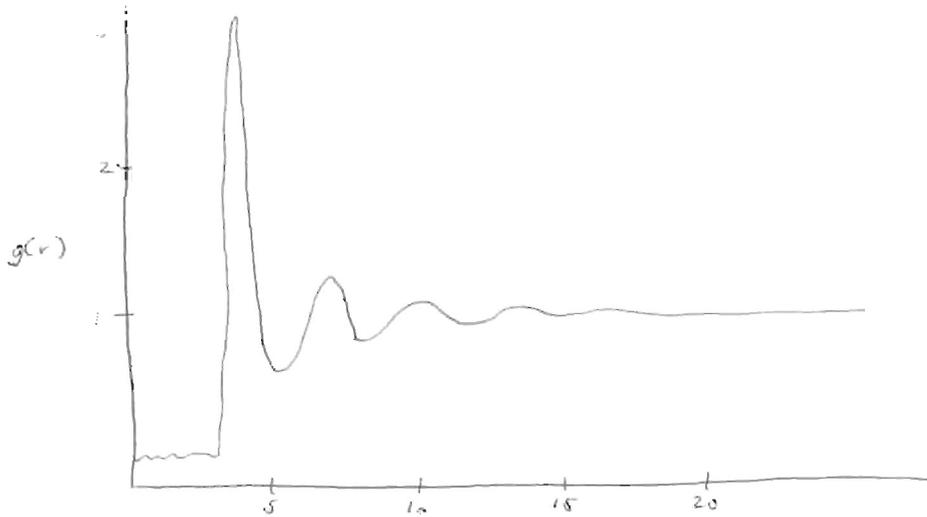**BONDING (4 problems, 50 points total)**

Question 1. Local structure: in 1973, Yarnell and co-workers determined the structure of argon at 85 K. The pair correlation function g(r) they found for this monoatomic substance is shown below:

a. What is the definition of the pair correlation function? Why does it tend to 1.0 at large r?

Consider the material in its stable phase at 85 K, and imagine a sphere with one of the atoms at the center of a sphere. A volume of the material can be defined between a sphere with radius r and a concentric sphere with radius r+dr. The pair correlation is defined

$$g(r) = \frac{1}{\rho} \frac{N(r, r+dr)}{V(r, r+dr)}$$

where ρ is the density of the material, N(r, r+dr) is the number of atoms in the volume between r and r+dr, and V(r,r+dr) is the volume.

g(r) is a useful quanitity because near the origin, the number of atoms in a shell of the sphere fluctuates largely based on the arrangement of the atoms. g(r) tends to 1.0 at large distances because the number of atoms per volume (N/V) becomes equal to the density far away from the origin. At far distances, the number of neighbors is so great that their individual contributions to N/V do not appear as unique peaks in g(r).

b. What is the state of argon at 85 K? Is it a solid, a liquid, or a gas, and why?

The peaks indicate some nonrandom arrangement of the atoms is present, which means the material is not a gas. If the peaks were discrete, the distance to the neighbors would be exact, and the material would be a solid. Since the function is continuous and the peaks have nonzero width, the material must be a liquid at 85 K.

c. What is your estimate for the diameter of an argon atom?

The distance from the r = 0 to the beginning of the first peak in the g(r) plot is the average distance from the center of one atom to the center of the nearest neighbor atom.

$2 R \approx 3.2$ Å
diameter = $2 R \approx 3.2$ Å

This diameter is somewhat larger than expected. Argon is a noble gas with electronic configuration [Na] $3s^2 3p^6$. If the material is a liquid, however, the distance from the orgin of g(r) to the first peak may not be the distance from the center of one hard sphere touching an adjacent hard sphere.

d. What do the peaks on the g(r) shown above represent?

The peaks represent large fluctuations from the average density of the material. The large fluctuations at short distances from the origin occur because the closest neighbors reside at regular intervals from the atom at the origin. Areas of empty space result in troughs in g(r), and areas where a nearest neighbor resides is a peak in N/V.   The peaks show the first through the fourth nearest neighbors from the origin.

e. Why does the pair-correlation function flatten beyond 15-20 Å?

g(r) flattens because distinct neighbors are not present at long range in the liquid. The number of neighbors per volume in the shell at (r,r+dr) is equal to the density.
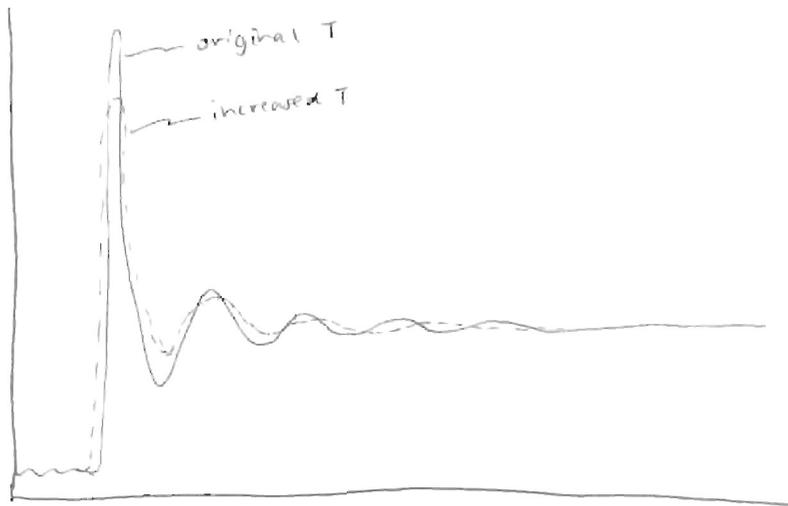
f. How can you calculate the number of first-neighbors around an argon atom at 85 K?

$$N = \rho \int_0^R g(r) 4\pi r^2 dr$$

R = 5 Å, which is the end of the first solvation shell.

g. In which ways would the g(r) (reproduced below) change if the temperature were to increase by a small amount (small enough that the system doesn't undergo a phase transition)?

The peaks would shorten and broaden.

h. How would the pair-correlation function for argon look like for the two other states not considered in point b. ? (label each of the two pair-correlation functions either as solid, liquid, or gas)
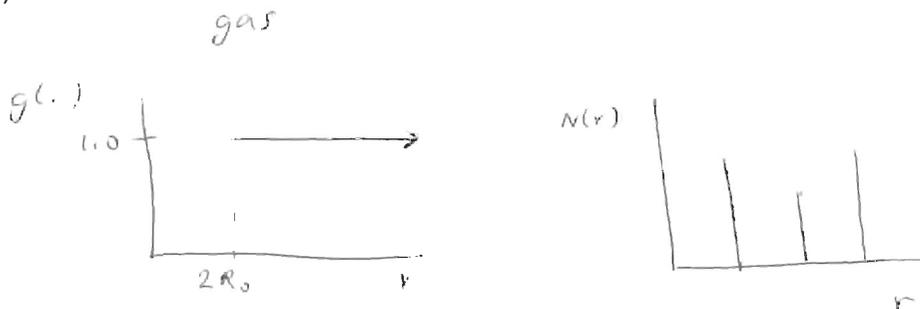
Question 2. Nematic liquid crystals

a. What characterizes a nematic liquid crystal? How is it different from a cholesteric liquid crystal, or from a smectic one? Discuss these differences in terms of orientation and translation order parameters, both long-range and short-range.

The translation (Σ) and orientation (S) order parameters are given by

$$\Sigma = \left\langle \cos\left(\frac{2\pi z}{a} \right) \right\rangle \qquad S = \frac{3\langle \cos^2 \theta \rangle - 1}{2}$$

Nematic phases show strong translational order in short range. They show strong orientational order in long range due to a unique axis along which the mesogen orient themselves. The nematic phases have some, but weaker orientational order at short range. Cholesteric phases are similar to nematic phases, but in cholesteric phases, the mesogen orientation twists along the unique axis. Cholesteric show orientational order at short range but little orientational order at long range. Cholestric phases show little translational order. Smectic phases have long range translational and orientational order.

b. The orientation order parameter S for a neumatic liquid crystal is (given above), where θ is the angle between a mesogen and the average preferred orientation $\hat{n}$, and the angular brackets represent an average over all the mesogens in the sample. Show what the order parameter S will be if all the mesogens are oriented perfectly in the direction $\hat{n}$, and what will it be if they are randomly oriented (derive explicitly your result).

mesogens orient perfectly in $\hat{n}$ → $\theta = 0$
$$\cos^2 \theta = 1$$
$$\therefore S = 1$$

mesogens randomly oriented → $\theta = 0 \dots 90\,°$
$$\cos \theta = +1 \dots 0$$
$$\cos^2 \theta = +1 \dots 0$$
average of $\cos^2 \theta = \langle \cos^2 \theta \rangle = 0.5$
$$\therefore S = 0$$

c. Suppose that a material goes through 4 phases as temperature is increased: first it is a solid, then a smectic liquid crystal, then a nematic liquid crystal, and finally an isotropic liquid. How will the orientation order parameter change with temperature (the phase-transition temperatures are labeled as T1, T2, and T3)?
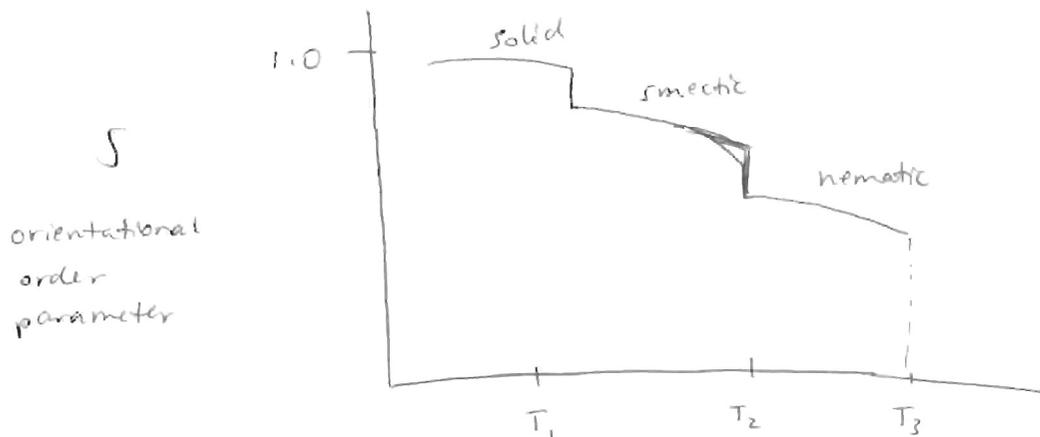
Question 3. X-ray diffraction
a. Suppose we have a real space Bravais lattice with principal crystallographic vectors $\vec{a}_1, \vec{a}_2$, and $\vec{a}_3$. What condition does the wavevector $\vec{k}$, of a plane wave $A\exp(i\vec{k} \cdot \vec{r})$ must satisfy so that the planewave has the same value at every point $(l, m, n) = l\vec{a}_1 + m\vec{a}_2 + n\vec{a}_3$ of the Bravais lattice? (As always, demonstrate your statement)

The wavevector at any point $\vec{r}$ must be the same at every other point found by a translation $\vec{R}$, which is a linear combination of the cell vectors

$$\vec{R} = l\vec{a}_1 + m\vec{a}_2 + n\vec{a}_3$$

$$A\exp(i\vec{k} \cdot \vec{r}) = A\exp(i\vec{k} \cdot (\vec{r} + \vec{R}))$$

$$A\exp(i\vec{k} \cdot \vec{r}) = A\exp[(i\vec{k} \cdot \vec{r})(i\vec{k} \cdot \vec{R})]$$

$$\exp(i\vec{k} \cdot \vec{R}) = 1$$

$$\vec{k} \cdot \vec{R} = 2\pi n$$
$$\uparrow$$
$$\text{integer}$$

b. Explain how the Laue conditions arise for constructive interference of a plane wave incident on a monoatomic crystal that has one atom at each point of the Bravais lattice $(l,m,n) = l\vec{a}_1 + m\vec{a}_2 + n\vec{a}_3$

c. The Ewald construction can be used to determine if Laue diffraction will be present of not in a given sample. Describe, first in words, and only at the end with a figure, the Ewald construction, its relation to the incoming and outgoing versors for the diffracted x-ray beams, and the reciprocal lattice of the crystal you are investigating.

The incoming xrays to a sample may be represented by a vector of length $2\pi/\lambda$ and direction given by a versor (vector of unit length) $\mathbf{S_0}$. Outgoing xrays from a sample may be represented by a vector of length $2\pi/\lambda$ and direction given by a versor $\mathbf{S}$. Laue conditions state that when the difference between incoming and outgoing vectors is equal to an integer number of wavelengths, diffraction occurs. $\mathbf{d}^*$ represents $\mathbf{S}$-$\mathbf{S_0}$ vectors giving constructive interference. $\mathbf{d}^*$ vectors must represent orientations in the crystal allowing some integer combination of wavelengths.

To figure out what orientations give rise to integer number of wavelengths, consider an array of points in three dimensions. Each point has an index (h k l) that represents how many integer number of $2\pi/\lambda$ lengths occur in the three orthogonal directions. The array of points is the reciprocal space. Now imagine the vector $\mathbf{S}$ in the reciprocal space. If $\mathbf{S}$ has a constant length and is rotated in every direction with one end as a pivot, it creates a sphere of all possible points a vector of $2\pi/\lambda$ can make. We are interested in finding the places where $\mathbf{S}$-$\mathbf{S_0}$ give rise to diffraction. The places where the sphere intersects the points of reciprocal space are the points that are integer numbers of $2\pi/\lambda$. These points are the endpoints of the $\mathbf{d}^*$ vectors. The points or indices (h k l) in reciprocal space represent real space directions in the crystal that have give rise to diffraction in a sample.
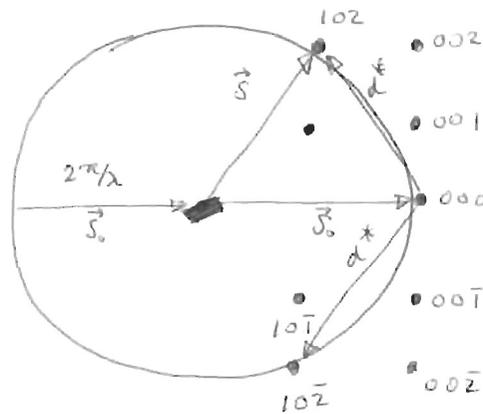
d. Why do we use monochromatic x-rays in a Debye-Scherrer experiment?

To measure diffracted rays from a sample, one must either look at the sample from a range of views but with a single wavelength or one must look from one direction and monitor a variety of wavelengths in order to determine characteristic **d** spacings. The Debye-Scherrer experiment uses the first approach. A camera circles a sample of crystalline powder irradiated with x-rays. The powder contains many orientations of the crystals, and diffracted beams occur in many directions. Using Bragg's Law $n\lambda = 2\,d\,sin\theta$, many angles θ are known, λ is constant, and thus d can be solved for.

Question 4. Symmetry constraints of physical properties: at a well-known Institute of Technology in the Northeast of the United States, Prof. Superman, Prof. Laue, and two UROP students are busy at work. Prof. Superman has brought a crystal of kryptonite and gone off to greater glories. Prof. Laue has given it a glance (Prof. Laue emits x-rays in his spare time) and proclaimed that kryptonite is metallic and has point group made only by a 4-fold rotation axis and a mirror plane perpendicular to that axis. The UROPs are asked to figure out what the symmetry properties of the electrical conductivity tensor $\underline{\underline{\sigma}}$ are ($\underline{\underline{\sigma}}$ relates an applied field to a current density via $\vec{j} = \underline{\underline{\sigma}}\vec{E}$, i.e. $j_i = \sigma_{ik} E_k$), write a convincing explanation for it, and invoke a clear statement of the Neumann principle in the process. Can you help them out and grant them a well deserved break?

Neumann's principle states that the magnitude of a physical property of a material, when measured along a specific direction, is unchanged when the material undergoes a transformation by a symmetry operation from a symmetry element in it's point group.

This means that the conductivity tensor σ_{ik} must be equal to the conductivity tensor σ_{ik}' that results after applying one of the crystal's symmetry operations. The method of direct inspection allows us to obtain σ_{ik}' by seeing what happens to the transformation of the X axes. from σ_{ik} v

$$X_1 \rightarrow X_2 \qquad X_1' = X_2$$
$$X_2 \rightarrow -X_1 \qquad X_2' = -X_1$$
$$X_3 \rightarrow X_3 \qquad X_3' = X_3$$

by Neumann

σ_{ik}	$X_i X_k$	$X_i' X_k'$	σ_{ik}'	$=$	σ_{ik}
σ_{11}	$X_1 X_1$	$X_1' X_1' = X_2 X_2$	σ_{22}	$=$	σ_{11}
σ_{12}	$X_1 X_2$	$X_1' X_2' = X_2(-X_1)$	$-\sigma_{21}$	$=$	σ_{12}
σ_{13}	$X_1 X_3$	$X_1' X_3' = X_2 X_3$	σ_{23}	$=$	$\sigma_{13} = 0$
σ_{21}	$X_2 X_1$	$X_2' X_1' = -X_1 X_2$	$-\sigma_{12}$	$=$	σ_{21}
σ_{22}	$X_2 X_2$	$X_2' X_2' = (-X_1)(-X_1)$	σ_{11}	$=$	σ_{22}
σ_{23}	$X_2 X_3$	$X_2' X_3' = (-X_1)(X_3)$	$-\sigma_{13}$	$=$	$\sigma_{23} = 0$
σ_{31}	$X_3 X_1$	$X_3' X_1' = (X_3)(X_2)$	σ_{32}	$=$	σ_{31}
σ_{32}	$X_3 X_2$	$X_3' X_2' = X_3(-X_1)$	$-\sigma_{31}$	$=$	σ_{32}
σ_{33}	$X_3 X_3$	$X_3' X_3' = X_3 X_3$	σ_{33}	$=$	σ_{33}

$$\sigma_{ik} = \begin{bmatrix} \sigma_{11} & \sigma_{12} & 0 \\ -\sigma_{12} & \sigma_{11} & 0 \\ 0 & 0 & \sigma_{33} \end{bmatrix}$$

$$\begin{pmatrix} -\sigma_{31} & = & \sigma_{31} \\ -\sigma_{31} & = & \sigma_{32} \end{pmatrix} = 0$$

$\boxed{\sigma_1}$

$$x_1 \to x_1 \qquad x_1' = x_1$$
$$x_2 \to x_2 \qquad x_2' = x_2$$
$$x_3 \to -x_3 \qquad x_3' = -x_3$$

σ_{ik}	$x_i x_k$	$x_i' x_k'$	σ_{ik}'	$=$	σ_{ik}
σ_{11}	$x_1 x_1$	$x_1' x_1' = x_1 x_1$	σ_{11}	$=$	σ_{11}
σ_{12}	$x_1 x_2$	$x_1' x_2' = x_1 x_2$	σ_{12}	$=$	σ_{12}
σ_{13}	$x_1 x_3$	$x_1' x_3' = x_1(-x_3)$	$-\sigma_{13}$	$=$	$\sigma_{13} = 0$
σ_{21}	$x_2 x_1$	$x_2' x_1' = x_2 x_1$	σ_{21}	$=$	σ_{21}
σ_{22}	$x_2 x_2$	$x_2' x_2' = x_2 x_2$	σ_{22}	$=$	σ_{22}
σ_{23}	$x_2 x_3$	$x_2' x_3' = x_2(-x_3)$	$-\sigma_{23}$	$=$	$\sigma_{23} = 0$
σ_{31}	$x_3 x_1$	$x_3' x_1' = -x_3 x_1$	$-\sigma_{31}$	$=$	$\sigma_{31} = 0$
σ_{32}	$x_3 x_2$	$x_3' x_2' = (-x_3)(x_2)$	$-\sigma_{32}$	$=$	$\sigma_{32} = 0$
σ_{33}	$x_3 x_3$	$x_3' x_3' = (-x_3)(-x_3)$	σ_{33}	$=$	σ_{33}

$$\sigma_{ik} = \begin{bmatrix} \sigma_{11} & \sigma_{12} & 0 \\ \sigma_{21} & \sigma_{21} & 0 \\ 0 & 0 & \sigma_{33} \end{bmatrix}$$

combining the results from the 4-fold axis and the perpendicular mirror plane shows that only three unique quantities remain in the conductivity tensor

$$\sigma_{ik} = \begin{bmatrix} \sigma_{11} & \sigma_{12} & 0 \\ -\sigma_{12} & \sigma_{11} & 0 \\ 0 & 0 & \sigma_{33} \end{bmatrix}$$