
Crystal phases

Structured phases



Structured phases

Crystal states

Oscillator Hamiltonian

One-particle density

Gaussian integrals

One-particle density

Plot of density

- Let us return to the basic pair-interaction energy

$$H = \sum_{i=1}^N \frac{p_i^2}{2m} + \frac{1}{2} \sum'_{i,j} V(\vec{r}_i - \vec{r}_j).$$

- We know from experience that at sufficiently low temperatures, this does lead to the formation of crystals.

Structured phases

Structured phases

Crystal states

Oscillator Hamiltonian

One-particle density

Gaussian integrals

One-particle density

Plot of density

- Let us return to the basic pair-interaction energy

$$H = \sum_{i=1}^N \frac{p_i^2}{2m} + \frac{1}{2} \sum'_{i,j} V(\vec{r}_i - \vec{r}_j).$$

- We know from experience that at sufficiently low temperatures, this does lead to the formation of crystals.
- For any phase, it is useful to know the one-particle density

$$n_1(\vec{x}) = \langle \hat{n}_1(\vec{x}) \rangle, \quad \hat{n}_1(\vec{x}) = \sum_{i=1}^N \delta(\vec{x} - \vec{r}_i).$$

Structured phases

Structured phases

Crystal states

Oscillator Hamiltonian

One-particle density

Gaussian integrals

One-particle density

Plot of density

- Let us return to the basic pair-interaction Hamiltonian

$$H = \sum_{i=1}^N \frac{p_i^2}{2m} + \frac{1}{2} \sum'_{i,j} V(\vec{r}_i - \vec{r}_j).$$

- We know from experience that at sufficiently low temperatures, this does lead to the formation of crystals. prime means i is not equal to j
- For any phase, it is useful to know the one-particle density

$$n_1(\vec{x}) = \langle \hat{n}_1(\vec{x}) \rangle, \quad \hat{n}_1(\vec{x}) = \sum_{i=1}^N \delta(\vec{x} - \vec{r}_i).$$

- In a liquid or a vapor, we know that

$$n_1(\vec{x}) = n,$$

which is independent of \vec{x} .

- But what is the form of $n_1(\vec{x})$ for a crystal?



Crystal states

Structured phases

Crystal states

Oscillator Hamiltonian

One-particle density

Gaussian integrals

One-particle density

Plot of density

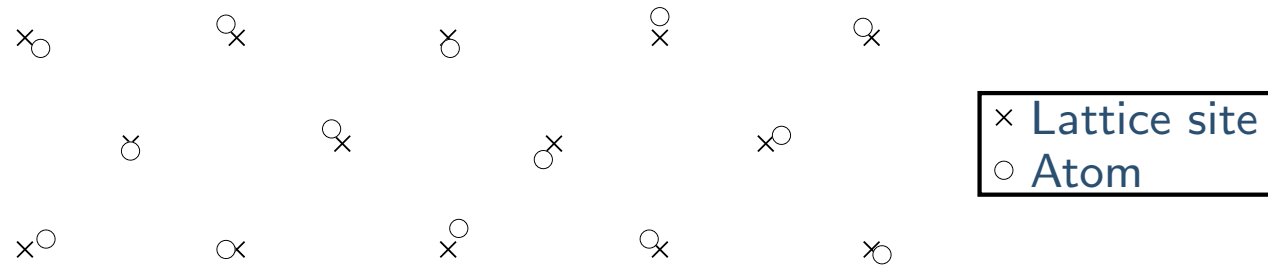
- In the case of a crystal, we can use information on the *state* of the system to rewrite the energy.



Crystal states

- Structured phases
- Crystal states**
- Oscillator Hamiltonian
- One-particle density
- Gaussian integrals
- One-particle density
- Plot of density

- In the case of a crystal, we can use information on the *state* of the system to rewrite the Hamiltonian.
- The characteristic feature of crystal states is that, at any given instant, the atoms are never very far from the lattice sites of an ideal crystal:





Crystal states

Structured phases

Crystal states

Oscillator Hamiltonian

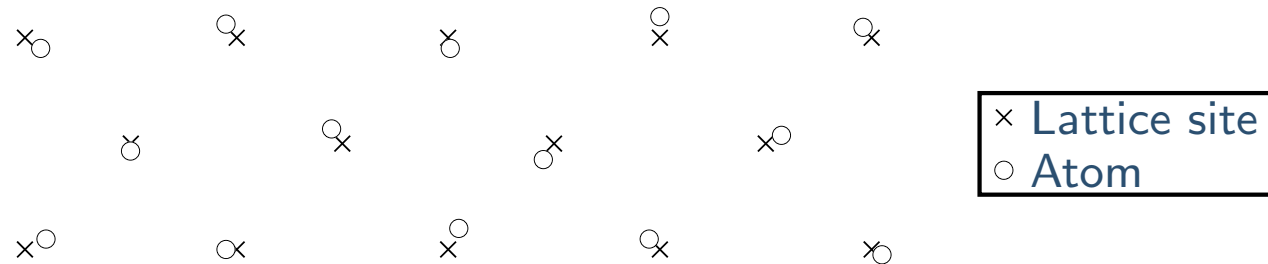
One-particle density

Gaussian integrals

One-particle density

Plot of density

- In the case of a crystal, we can use information on the *state* of the system to rewrite the Hamiltonian.
- The characteristic feature of crystal states is that, at any given instant, the atoms are never very far from the lattice sites of an ideal crystal:



- The position of atom i at any given instant is conveniently written as

$$\vec{r}_i = \vec{R}_i + \vec{u}_i,$$

where \vec{R}_i is the position of an ideal lattice site and \vec{u}_i is the displacement of the atom from that site.



Crystal states

Structured phases

Crystal states

Oscillator Hamiltonian

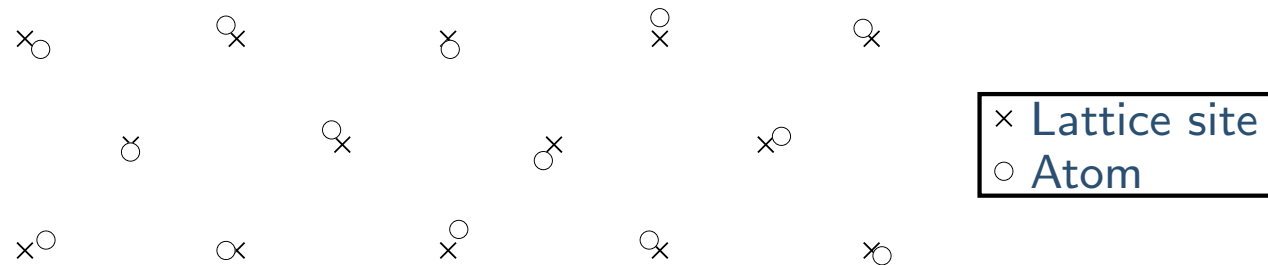
One-particle density

Gaussian integrals

One-particle density

Plot of density

- In the case of a crystal, we can use information on the *state* of the system to rewrite the Hamiltonian.
- The characteristic feature of crystal states is that, at any given instant, the atoms are never very far from the lattice sites of an ideal crystal:



- The position of atom i at any given instant is conveniently written as

$$\vec{r}_i = \vec{R}_i + \vec{u}_i,$$

where \vec{R}_i is the position of an ideal lattice site and \vec{u}_i is the displacement of the atom from that site.

- These have the mean values

$$\langle \vec{R}_i \rangle = \vec{R}_i, \quad \langle \vec{u}_i \rangle = 0, \quad \therefore \langle \vec{r}_i \rangle = \vec{R}_i.$$



Oscillator Hamiltonian

Structured phases

Crystal states

Oscillator Hamiltonian

One-particle density

Gaussian integrals

One-particle density

Plot of density

- Given this observation, the instantaneous energy of atom i for small displacements \vec{u}_i is

$$\frac{p_i^2}{2m} + \text{const} + \frac{1}{2}m\omega^2 u_i^2,$$

where the constant is the potential energy of the atom in a perfect crystal.

- The last term comes from a mean-field view, in which every atom is assigned the same oscillation frequency ω (i.e., the Einstein model)
 $V(\mathbf{r}_{ij}) \sim V(\mathbf{R}_{ij}) + u^2 V''(\mathbf{R}_{ij})$.



Oscillator Hamiltonian

Structured phases

Crystal states

Oscillator Hamiltonian

One-particle density

Gaussian integrals

One-particle density

Plot of density

- Given this observation, the instantaneous energy of atom i for small displacements \vec{u}_i is

$$\frac{p_i^2}{2m} + \text{const} + \frac{1}{2}m\omega^2 u_i^2,$$

where the constant is the potential energy of the atom in a perfect crystal.

- The last term comes from a mean-field view, in which every atom is assigned the same oscillation frequency ω (i.e., the Einstein model).
- The approximate Hamiltonian of the crystal is then

$$H = \text{const} + \sum_{i=1}^N \frac{p_i^2}{2m} + \sum_{i=1}^N \frac{1}{2}m\omega^2 u_i^2.$$

One-particle density

- Structured phases
- Crystal states
- Oscillator Hamiltonian
- One-particle density
- Gaussian integrals
- One-particle density
- Plot of density

- The classical one-particle density is hence

$$\langle \hat{n}_1(\vec{x}) \rangle = \frac{\int d\Gamma \sum_i \delta(\vec{x} - \vec{R}_i - \vec{u}_i) \exp(-\beta H)}{\int d\Gamma \exp(-\beta H)},$$

where $d\Gamma$ is the phase-space element

$$d\Gamma \equiv d^3p_1 \cdots d^3p_N d^3u_1 \cdots d^3u_N.$$

One-particle density

- Structured phases
- Crystal states
- Oscillator Hamiltonian
- One-particle density
- Gaussian integrals
- One-particle density
- Plot of density

- The classical one-particle density is hence

$$\langle \hat{n}_1(\vec{x}) \rangle = \frac{\int d\Gamma \sum_i \delta(\vec{x} - \vec{R}_i - \vec{u}_i) \exp(-\beta H)}{\int d\Gamma \exp(-\beta H)},$$

where $d\Gamma$ is the phase-space element

$$d\Gamma \equiv d^3p_1 \cdots d^3p_N d^3u_1 \cdots d^3u_N.$$

- Since $\hat{n}_1(\vec{x})$ does not contain \vec{p}_i , the momentum integrals cancel, leaving

$$n_1(\vec{x}) = \frac{\int d^3u_1 \cdots \int d^3u_N \sum_i \delta(\vec{x} - \vec{R}_i - \vec{u}_i) \prod_j \exp(-m\omega^2 u_j^2 / 2k_B T)}{\int d^3u_1 \cdots \int d^3u_N \prod_i \exp(-m\omega^2 u_i^2 / 2k_B T)}.$$



One-particle density

- Structured phases
- Crystal states
- Oscillator Hamiltonian
- One-particle density**
- Gaussian integrals
- One-particle density
- Plot of density

- The classical one-particle density is hence

$$\langle \hat{n}_1(\vec{x}) \rangle = \frac{\int d\Gamma \sum_i \delta(\vec{x} - \vec{R}_i - \vec{u}_i) \exp(-\beta H)}{\int d\Gamma \exp(-\beta H)},$$

where $d\Gamma$ is the phase-space element

$$d\Gamma \equiv d^3 p_1 \cdots d^3 p_N d^3 u_1 \cdots d^3 u_N.$$

- Since $\hat{n}_1(\vec{x})$ does not contain \vec{p}_i , the momentum integrals cancel, leaving

$$n_1(\vec{x}) = \frac{\int d^3 u_1 \cdots \int d^3 u_N \sum_i \delta(\vec{x} - \vec{R}_i - \vec{u}_i) \prod_j \exp(-m\omega^2 u_j^2 / 2k_B T)}{\int d^3 u_1 \cdots \int d^3 u_N \prod_i \exp(-m\omega^2 u_i^2 / 2k_B T)}.$$

- Here the denominator is a product of N integrals of the form

$$\int \exp\left(-\frac{m\omega^2 u^2}{2k_B T}\right) d^3 u = 4\pi \int_0^\infty u^2 \exp\left(-\frac{m\omega^2 u^2}{2k_B T}\right) du.$$

Gaussian integrals

- Structured phases
- Crystal states
- Oscillator Hamiltonian
- One-particle density
- Gaussian integrals**
- One-particle density
- Plot of density

- Upon making the substitution $v = m\omega^2 u^2 / 2k_B T$, we obtain

$$\begin{aligned}\int \exp\left(-\frac{m\omega^2 u^2}{2k_B T}\right) d^3 u &= 4\pi \int_0^\infty u^2 \exp\left(-\frac{m\omega^2 u^2}{2k_B T}\right) du \\ &= \frac{4\pi}{2} \left(\frac{2k_B T}{m\omega^2}\right)^{3/2} \int_0^\infty v^{1/2} \exp(-v) dv \\ &= 2\pi \left(\frac{2k_B T}{m\omega^2}\right)^{3/2} \frac{\sqrt{\pi}}{2} \\ &= \left(\frac{2\pi k_B T}{m\omega^2}\right)^{3/2} .\end{aligned}$$

Gaussian integrals

- Structured phases
- Crystal states
- Oscillator Hamiltonian
- One-particle density
- Gaussian integrals**
- One-particle density
- Plot of density

- Upon making the substitution $v = m\omega^2 u^2 / 2k_B T$, we obtain

$$\begin{aligned}\int \exp\left(-\frac{m\omega^2 u^2}{2k_B T}\right) d^3 u &= 4\pi \int_0^\infty u^2 \exp\left(-\frac{m\omega^2 u^2}{2k_B T}\right) du \\ &= \frac{4\pi}{2} \left(\frac{2k_B T}{m\omega^2}\right)^{3/2} \int_0^\infty v^{1/2} \exp(-v) dv \\ &= 2\pi \left(\frac{2k_B T}{m\omega^2}\right)^{3/2} \frac{\sqrt{\pi}}{2} \\ &= \left(\frac{2\pi k_B T}{m\omega^2}\right)^{3/2}.\end{aligned}$$

- All of the integrals in the numerator are the same as this, except for one delta-function integral yielding a Gaussian function.

One-particle density

- Structured phases
- Crystal states
- Oscillator Hamiltonian
- One-particle density
- Gaussian integrals
- One-particle density
- Plot of density

- The one-particle density is thus of the form

$$n_1(\vec{x}) = \langle \hat{n}_1(\vec{x}) \rangle = \sum_{i=1}^N f(\vec{x} - \vec{R}_i),$$

in which $f(\vec{x})$ is the normalized Gaussian function

$$f(\vec{x}) = \left(\frac{m\omega^2}{2\pi k_B T} \right)^{3/2} \exp\left(-\frac{m\omega^2 x^2}{2k_B T} \right).$$

One-particle density

- Structured phases
- Crystal states
- Oscillator Hamiltonian
- One-particle density
- Gaussian integrals
- One-particle density**
- Plot of density

- The one-particle density is thus of the form

$$n_1(\vec{x}) = \langle \hat{n}_1(\vec{x}) \rangle = \sum_{i=1}^N f(\vec{x} - \vec{R}_i),$$

in which $f(\vec{x})$ is the normalized Gaussian function

$$f(\vec{x}) = \left(\frac{m\omega^2}{2\pi k_B T} \right)^{3/2} \exp\left(-\frac{m\omega^2 x^2}{2k_B T} \right).$$

- Here we can identify the width of the Gaussian as

$$\sigma = \sqrt{\frac{k_B T}{m\omega^2}} \quad \Rightarrow \quad f(\vec{x}) = \left(\frac{1}{\sqrt{2\pi}\sigma} \right)^3 \exp\left(-\frac{x^2}{2\sigma^2} \right).$$

One-particle density

- Structured phases
- Crystal states
- Oscillator Hamiltonian
- One-particle density
- Gaussian integrals
- One-particle density**
- Plot of density

- The one-particle density is thus of the form

$$n_1(\vec{x}) = \langle \hat{n}_1(\vec{x}) \rangle = \sum_{i=1}^N f(\vec{x} - \vec{R}_i),$$

in which $f(\vec{x})$ is the normalized Gaussian function

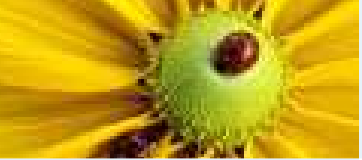
$$f(\vec{x}) = \left(\frac{m\omega^2}{2\pi k_B T} \right)^{3/2} \exp\left(-\frac{m\omega^2 x^2}{2k_B T} \right).$$

- Here we can identify the width of the Gaussian as

$$\sigma = \sqrt{\frac{k_B T}{m\omega^2}} \quad \Rightarrow \quad f(\vec{x}) = \left(\frac{1}{\sqrt{2\pi}\sigma} \right)^3 \exp\left(-\frac{x^2}{2\sigma^2} \right).$$

- Since $\int f(\vec{x}) d^3x = 1$, we obtain the expected result

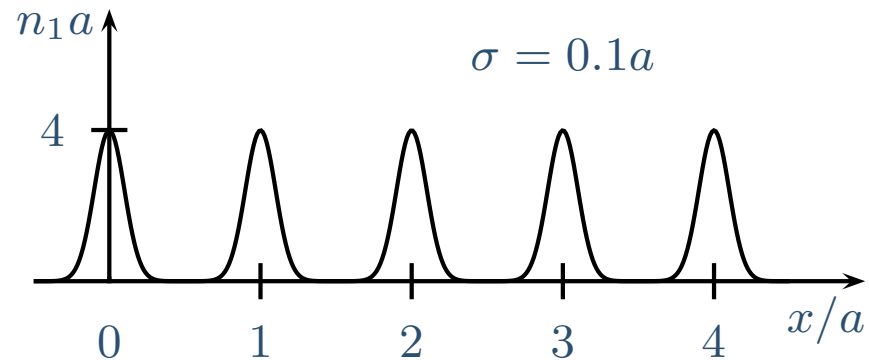
$$\int n_1(\vec{x}) d^3x = N.$$



Plot of density

Structured phases
Crystal states
Oscillator Hamiltonian
One-particle density
Gaussian integrals
One-particle density
Plot of density

- A plot of $n_1(x)$ is shown below for a one-dimensional crystal with lattice constant a :



- In computer simulations, if σ has too large a value, the crystal melts.

More accurate estimate of the lattice energy

- $r_i = R_i + u_i$
- $E = \sum_{i<j} V(r_i - r_j) \cong E_0 + U'', E_0 = \sum_{i<j} V(R_i - R_j)$
- $U'' = \sum_{i<j} V''(R_i - R_j)(u_i - u_j)^2/2$
- There are no first derivative terms because the net force is zero, the solid is in equilibrium.
- The energy involves products of u_i and u_j
- The partition function $Z = \int \prod_i dr_i e^{-\beta E} = e^{-\beta E_0} Z'$,
- $Z' = \int \prod_i du_i e^{-\beta U''}$
- It is difficult to calculate averages because of the coupling U'' .

More accurate estimate of the lattice energy

- $U'' = \sum_{i < j} V''(R_i - R_j)(u_i - u_j)^2 / 2$
- The energy involves products of u_i and u_j .
- Now do Fourier transform: $u(q) = \sum_j u_j e^{iq \cdot R_j} / \sqrt{N}$ for N lattice sites.
- $U'' = \sum_q |u(q)|^2 m\omega_q^2$
- $m\omega_q^2 = \sum_j V''(R_j)(1 - \cos q \cdot R_j)$
- The energy does not involve products of u_p and u_q for different p and q
- For small q, $\omega_q^2 \propto q^2$

Averages of the Fourier modes

- The partition function
- $Z = \int \prod_i du_i e^{-\beta E} = e^{-\beta E_0} Z'$
- $Z' = \int \prod_k du_k e^{-\beta \sum_q |u(q)|^2 m \omega_q^2}$
- $= \prod_k \int du_k e^{-\beta m \omega_k^2 |u(k)|^2}$
- $Z' = \prod_k [\pi / (\beta m \omega_k^2)]^{1/2}$
- $\langle |u(q)|^2 \rangle = -\partial \ln Z / \partial (\beta m \omega_q^2) = kT / 2m \omega^2(q)$

Position fluctuation

- $\langle [u(0)-u(R)]^2 \rangle \propto \int d^D q e^{iq \cdot R} \langle |u(q)|^2 \rangle$
- This is a measure of the long range order of the system.
- To proceed, look at the Fourier transform
- $\langle |u(q)|^2 \rangle = kT/2m\omega^2(q)$
- For large R, contribution comes from small q
- $\langle [u(0)-u(R)]^2 \rangle \propto \int d^D q e^{iq \cdot R} kT/q^2$
- This is divergent for D less than or equal to 2 for large R.
- For D=2, $\langle [u(0)-u(R)]^2 \rangle \propto \ln R$
- **No position long range order for spatial dimension less than or equal to 2.**