PHY 770 -- Statistical Mechanics
12:00* - 1:45 PM TR Olin 107

Instructor: Natalie Holzwarth (Olin 300)
Course Webpage: http://www.wfu.edu/~natalie/s14phy770

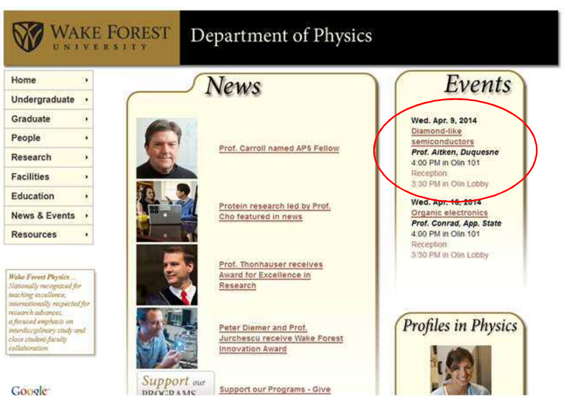
Lecture 20

Chap. 9 – Transport coefficients

- ❑ The Boltzmann equation
- ❑ Treatment of the collision term
- ❑ Examples

*Partial make-up lecture -- early start time

11	Tue: 02/18/2014	Chap. 5	Equilibrium Statistical Mechanics	#11	02/27/2014
12	Thur: 02/20/2014	Chap. 5	The Ising model (class 12-1:45 PM)	#12	02/27/2014
	Tue: 02/25/2014		NAWH out of town -- no class		
13	Thur: 02/27/2014	Chap. 6	Grand partition function (class 12-1:45 PM)		
	Tue: 03/04/2014	*APS Meeting*	Take-home exam (no class meeting)		
	Thur: 03/06/2014	*APS Meeting*	Take-home exam (no class meeting)		
	Tue: 03/11/2014		Spring break (no class meeting)		
	Thur: 03/13/2014		Spring break (no class meeting)		
14	Tue: 03/18/2014	Chap. 6	Fermi and Bose particles (class 12-1:45 PM; Exam due)	#13	03/25/2014
15	Thur: 03/20/2014	Chap. 6	Interacting particles (class 12-1:45 PM)	#14	03/25/2014
16	Tue: 03/25/2014	Chap. 7	Langevin equation (class 12-1:45 PM)	#15	04/01/2014
17	Thur: 03/27/2014	Chap. 7	Fokker-Planck equation (class 12-1:45 PM)	#16	04/03/2014
18	Tue: 04/01/2014	Chap. 7	Linear Response (class 12-1:45 PM)	#17	04/10/2014
19	Thur: 04/03/2014	Chap. 9	Transport theory (class 12-1:45 PM)	#18	4/10/2014
20	Tue: 04/08/2014	Chap. 9	The Boltzmann Equation (class 12-1:45 PM)	#19	4/10/2014
21	Thur: 04/10/2014	Chap. 9	The Boltzmann Equation (class 12-1:45 PM)	#20	4/17/2014
22	Tue: 04/15/2014		(class 12-1:45 PM)		
23	Thur: 04/17/2014		(class 12-1:45 PM)		
24	Tue: 04/22/2014		(class 12-1:45 PM)		
	Thur: 04/24/2014		Presentations Part I (class 11-1:45 PM)		
	Tue: 04/29/2014		Presentations Part II (class 11-1:45 PM)		



WFU Physics Colloquium

TITLE: Crystal Structure, Electronic Structure and Physicochemical Characterization of Multi-Cation Diamond-Like Semiconductors

SPEAKER: Professor Jennifer Aitken,

Department of Chemistry and Biochemistry, Duquesne University

TIME: Wednesday April 9, 2014 at 4:00 PM

PLACE: Room 101 Olin Physical Laboratory

Refreshments will be served at 3:30 PM in the Olin Lounge. All interested persons are cordially invited to attend.

ABSTRACT

Diamond-like semiconductors (DLSs) possess crystal structures that can be considered as derivatives of cubic or hexagonal diamond. DLSs are one of the few classes of solid-state compounds, for which all chemical compositions can be calculated and a set of possible structures postulated. The use of the many elements that can adopt tetrahedral coordination leads to a multitude of possible compounds, and solid solutions thereof, that can be exploited for physical property tuning. The compositional flexibility and structural simplicity of these materials provides an avenue to develop an intimate understanding of composition-property and structure-property correlations. This seminar will cover our recent progress toward this goal made during our search for DLSs with applications in non-linear optics and thermoelectrics, and as lithium ion conductors.

The Boltzmann equation

Define the distribution function $f(\mathbf{r},\mathbf{v},t)$:

$f(\mathbf{r},\mathbf{v},t)d^3r d^3v$ represents the number of particles in the 6 dimensional phase space about $\mathbf{r}$ and $\mathbf{v}$ at time t.

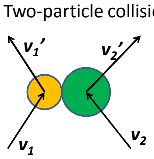
$\int f(\mathbf{r},\mathbf{v},t)d^3r d^3v = N$

$$\left(\frac{\partial}{\partial t} + \mathbf{v}\cdot\nabla_r + \frac{\mathbf{F}}{m}\cdot\nabla_v\right) f(\mathbf{r},\mathbf{v},t) = \left(\frac{\partial f}{\partial t}\right)_{coll}$$

Analysis of collision term

$$\left(\frac{\partial f}{\partial t}\right)_{coll} = \left(\frac{\Delta f}{\Delta t}\right)_{added} - \left(\frac{\Delta f}{\Delta t}\right)_{removed}$$

Two-particle collision events

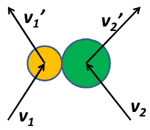


Conservation of momentum: $m_1\mathbf{v}_1 + m_2\mathbf{v}_2 = m_1\mathbf{v}_1' + m_2\mathbf{v}_2'$

Conservation of energy: $\frac{1}{2}m_1 v_1^2 + \frac{1}{2}m_2 v_2^2 = \frac{1}{2}m_1 v_1'^2 + \frac{1}{2}m_2 v_2'^2$

$\Rightarrow \quad |\mathbf{v}_1 - \mathbf{v}_2| = |\mathbf{v}_1' - \mathbf{v}_2'| \equiv g$

Two-particle collision events

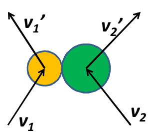


$$m_1\mathbf{v}_1 + m_2\mathbf{v}_2 = m_1\mathbf{v}_1' + m_2\mathbf{v}_2'$$
$$\frac{1}{2}m_1v_1^2 + \frac{1}{2}m_2v_2^2 = \frac{1}{2}m_1v_1'^2 + \frac{1}{2}m_2v_2'^2$$
$$|\mathbf{v}_1 - \mathbf{v}_2| = |\mathbf{v}_1' - \mathbf{v}_2'| \equiv g$$

Assumptions
- Only two-particle collisions considered
- Only elastic collisions considered
- Assume that force **F** does not effect collisions
- Assume that distribution function $f(\mathbf{r},\mathbf{v},t)$ is slowly varying in $\mathbf{r}$ within collision volume
- In a two-particle collision , the distribution functions for the two particles are independent (uncorrelated)

Analysis of collision term

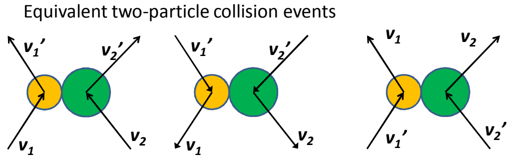
Two-particle collision events



$$\bar{\sigma}(\mathbf{v}_1,\mathbf{v}_2 \rightarrow \mathbf{v}_1',\mathbf{v}_2')\,dv_1^3 dv_2^3$$

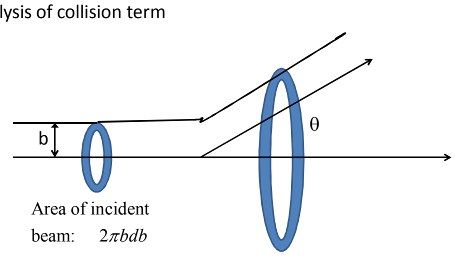
Denotes the number of particles per unit time and per unit flux of particles 1 incident on particles 2 with initial velocities $\mathbf{v}_1,\mathbf{v}_2$ and final velocities $\mathbf{v}_1', \mathbf{v}_2'$

Equivalent two-particle collision events



$$\bar{\sigma}(\mathbf{v}_1,\mathbf{v}_2 \rightarrow \mathbf{v}_1',\mathbf{v}_2') = \bar{\sigma}(-\mathbf{v}_1,-\mathbf{v}_2 \rightarrow -\mathbf{v}_1',-\mathbf{v}_2') = \bar{\sigma}(\mathbf{v}_1',\mathbf{v}_2' \rightarrow \mathbf{v}_1,\mathbf{v}_2)$$

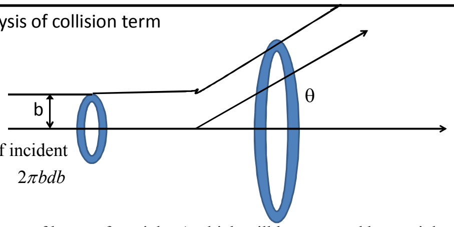
Analysis of collision term



As discussed in Appendix E of your textbook, the scattering cross section describes the effective area cut out of the incident beam by the scattering process.

$$\frac{d\sigma_{lab}}{d\Omega_{lab}} = \left|\frac{bdb}{\sin\theta_{lab}d\theta_{lab}}\right| \qquad \frac{d\sigma_{CM}}{d\Omega_{CM}} = \left|\frac{bdb}{\sin\theta_{CM}d\theta_{CM}}\right|$$

Analysis of collision term



Area of incident beam: $2\pi b db$

Volume of beam of particles 1 which will be scattered by particles 2 per unit time: $|\mathbf{v}_2 - \mathbf{v}_1| 2\pi b db$

$$\left(\frac{\partial f}{\partial t}\right)_{coll} = \left(\frac{\Delta f}{\Delta t}\right)_{added} - \left(\frac{\Delta f}{\Delta t}\right)_{removed}$$

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Analysis of collision term

$$\int \left(\frac{\Delta f}{\Delta t}\right)_{added} d^3v_1 = \int |\mathbf{v}_2 - \mathbf{v}_1| 2\pi b\ db\, f(\mathbf{r}, \mathbf{v}_1', t) f(\mathbf{r}, \mathbf{v}_2', t) d^3v_1' d^3v_2'$$

$$\int \left(\frac{\Delta f}{\Delta t}\right)_{removed} d^3v_1 = \int |\mathbf{v}_2 - \mathbf{v}_1| 2\pi b\ db\, f(\mathbf{r}, \mathbf{v}_1, t) f(\mathbf{r}, \mathbf{v}_2, t) d^3v_1 d^3v_2$$

Since $\frac{d\sigma_{CM}}{d\Omega_{CM}} = \left| \frac{bdb}{\sin\theta_{CM} d\theta_{CM}} \right| \quad \Rightarrow 2\pi b db = \frac{d\sigma_{CM}}{d\Omega_{CM}} d\Omega_{CM}$

Also note that $d^3v_1' d^3v_2' = d^3v_1 d^3v_2$

$$\left(\frac{\Delta f}{\Delta t}\right)_{added} - \left(\frac{\Delta f}{\Delta t}\right)_{removed} =$$

$$\int d\Omega_{CM} \int d^3v_2 |\mathbf{v}_2 - \mathbf{v}| \frac{d\sigma_{CM}}{d\Omega_{CM}} \left(f(\mathbf{r}, \mathbf{v}', t) f(\mathbf{r}, \mathbf{v}_2', t) - f(\mathbf{r}, \mathbf{v}, t) f(\mathbf{r}, \mathbf{v}_2, t) \right)$$

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Summary of results:

$$\left(\frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla_r + \frac{\mathbf{F}}{m} \cdot \nabla_v \right) f(\mathbf{r}, \mathbf{v}, t) = \left(\frac{\partial f}{\partial t}\right)_{coll}$$

With:

$$\left(\frac{\partial f}{\partial t}\right)_{coll} =$$

$$\int d\Omega_{CM} \int d^3v_2 |\mathbf{v}_2 - \mathbf{v}| \frac{d\sigma_{CM}}{d\Omega_{CM}} \left(f(\mathbf{r}, \mathbf{v}', t) f(\mathbf{r}, \mathbf{v}_2', t) - f(\mathbf{r}, \mathbf{v}, t) f(\mathbf{r}, \mathbf{v}_2, t) \right)$$

In the notation of your textbook:

$$\left(\frac{\partial f}{\partial t}\right)_{coll} = \int d\Omega_{CM} \int d^3v_2 g \sigma_{cm}(b, g) \left(f(\mathbf{r}, \mathbf{v}', t) f(\mathbf{r}, \mathbf{v}_2', t) - f(\mathbf{r}, \mathbf{v}, t) f(\mathbf{r}, \mathbf{v}_2, t) \right)$$

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Some rough estimates:

Number of collisions per second per unit volume for gas near equilibrium:

$$\mathcal{C} \approx \int d\Omega_{CM} \int d^3v d^3v_2 |\mathbf{v}_2 - \mathbf{v}| \sigma_{cm}(b,g) \left(f(\mathbf{r},\mathbf{v},t) f(\mathbf{r},\mathbf{v}_2,t) \right)$$

$$\approx \sigma_{tot} n^2 \left(\frac{\sqrt{m_1 m_2}}{2\pi kT} \right)^3 \int d^3v d^3v_2 |\mathbf{v}_2 - \mathbf{v}| e^{-(m_1 v^2 + m_2 v_2^2)/(2kT)}$$

$$\approx \sigma_{tot} n^2 \langle v \rangle \frac{4}{\sqrt{2\pi}} \qquad \text{where } \langle v \rangle = \sqrt{\frac{2kT}{m}} \quad \text{when all particles have same mass } m$$

Mean free path: $\lambda \approx \frac{n\langle v \rangle}{2\mathcal{C}} = \frac{1}{4}\sqrt{\frac{\pi}{2}} \frac{1}{n\sigma_{tot}}$

Collision time: $\tau \approx \frac{\lambda}{\langle v \rangle} = \frac{1}{4}\sqrt{\frac{\pi}{2}} \frac{1}{n\sigma_{tot}\langle v \rangle}$

Properties of Bolzmann equation

$$\left(\frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla_r + \frac{\mathbf{F}}{m} \cdot \nabla_v \right) f(\mathbf{r},\mathbf{v},t) = \left(\frac{\partial f}{\partial t} \right)_{coll}$$

Described the time evolution of the distribution of particles in six-dimensional phase space for a dilute gas. In the absence of external fields, the system should decay to equilibrium as shown by Boltzmann's H Theorem:

Define: $H(t) \equiv \int d^3r \int d^3v f(\mathbf{r},v,t) \ln\left(f(\mathbf{r},v,t) \right)$

Can show that $H(t)$ always decreases with collisions:

$$\frac{\partial H}{\partial t} = \int d^3r \int d^3v \frac{\partial f(\mathbf{r},v,t)}{\partial t} \left(\ln\left(f(\mathbf{r},v,t) \right) + 1 \right)$$

Properties of Bolzmann's H theorem continued (assume **F**=0)

$$\frac{\partial H}{\partial t} = \int d^3r \int d^3v \left(\left(-\mathbf{v} \cdot \nabla_r \right) f(\mathbf{r},\mathbf{v},t) + \left(\frac{\partial f}{\partial t} \right)_{coll} \right) \left(\ln\left(f(\mathbf{r},\mathbf{v},t) \right) + 1 \right)$$

$$\approx \int d^3r \int d^3v \left(\left(\frac{\partial f}{\partial t} \right)_{coll} \right) \left(\ln\left(f(\mathbf{r},\mathbf{v},t) \right) + 1 \right)$$

$$\frac{\partial H}{\partial t} \approx \int d^3r \int d^3v \left(\ln\left(f(\mathbf{r},\mathbf{v},t) \right) + 1 \right) \times$$
$$\int d\Omega_{CM} \int d^3v_2 g \sigma_{cm}(b,g) \left(f(\mathbf{r},\mathbf{v}',t) f(\mathbf{r},\mathbf{v}_2',t) - f(\mathbf{r},\mathbf{v},t) f(\mathbf{r},\mathbf{v}_2,t) \right)$$

Performing the same analysis but switching $\mathbf{v} \leftrightarrow \mathrm{v}_2$:

$$\frac{\partial H}{\partial t} \approx \int d^3r \int d^3v_2 \left(\ln\left(f(\mathbf{r},\mathbf{v}_2,t) \right) + 1 \right) \times$$
$$\int d\Omega_{CM} \int d^3v g \sigma_{cm}(b,g) \left(f(\mathbf{r},\mathbf{v}',t) f(\mathbf{r},\mathbf{v}_2',t) - f(\mathbf{r},\mathbf{v},t) f(\mathbf{r},\mathbf{v}_2,t) \right)$$

Properties of Bolzmann's H theorem continued (assume **F**=0)

Adding the two expressions together and switching variables, we find:

$$\frac{\partial H}{\partial t}=\frac{1}{4}\int d^3r\int d^3v\int d^3v_2\int d\Omega_{CM}\, g\,\sigma_{cm}(b,g)\;\left(f\,'f_2\,'-ff_2\right)\ln\left(\frac{ff_2}{f\,'f_2\,'}\right)$$

Note that for all real positive y, x $\quad \left(y-x\right)\ln\left(\frac{x}{y}\right)\leq 0$

Therefore $\frac{\partial H}{\partial t}\leq 0$

This implies that at equilibrium:

$$\frac{\partial H}{\partial t}\rightarrow 0 \quad \text{and} \quad ff_2 \rightarrow f\,'f_2'$$

Conservation laws implied by Boltzmann equation

Consider some quantity (mass, momentum, etc) associated with a particle of velocity **v** and position **r**: $\chi(\mathbf{r},\mathbf{v})$

If $\chi(\mathbf{r},\mathbf{v})$ is conserved during a collision $\left(\mathbf{v}_1,\mathbf{v}_2\rightarrow\mathbf{v}_1',\mathbf{v}_2'\right)$,

so that $\chi(\mathbf{r},\mathbf{v}_1)+\chi(\mathbf{r},\mathbf{v}_2)=\chi(\mathbf{r},\mathbf{v}_1')+\chi(\mathbf{r},\mathbf{v}_2')$, it is possible to show that:

$$\int d^3v\,\chi(\mathbf{r},\mathbf{v})\left(\frac{\partial f}{\partial t}\right)_{coll}=0$$

These results lead to identities involving the distribution function $f(\mathbf{r},\mathbf{v},t)$

Approximate solutions to Boltzmann equation

$$f(\mathbf{r},\mathbf{v},t)\approx f^0(\mathbf{r},\mathbf{v},t)\left(1+h(\mathbf{r},\mathbf{v},t)\right)$$

For free particle moving in 3 dimensions in thermal equilibrium:

$$f^0(\mathbf{r},\mathbf{v},t)=f^0(\mathbf{v})=n\left(\frac{m}{2\pi kT}\right)^{3/2}e^{-mv^2/(2kT)}$$

For $\mathbf{F}=0$:

$$\left(\frac{\partial}{\partial t}+\mathbf{v}\cdot\nabla_r\right)f(\mathbf{r},\mathbf{v},t)\approx f^0\left(\mathbf{v}\right)\left(\frac{\partial h}{\partial t}+\mathbf{v}\cdot\nabla_r h\right)$$

$$\left(\frac{\partial f}{\partial t}\right)_{coll}=\int d\Omega_{CM}\int d^3v_2\, g\,\sigma_{cm}(b,g)\;\left(f\left(\mathbf{r},\mathbf{v}',t\right)f\left(\mathbf{r},\mathbf{v}_2',t\right)-f\left(\mathbf{r},\mathbf{v},t\right)f\left(\mathbf{r},\mathbf{v}_2,t\right)\right)$$

$$\approx f^0\left(\mathbf{v}\right)\int d\Omega_{CM}\int d^3v_2\, g\,\sigma_{cm}(b,g)\,f^0\left(\mathbf{v}_2\right)\left(h\left(\mathbf{r},\mathbf{v}',t\right)+h\left(\mathbf{r},\mathbf{v}_2',t\right)-h\left(\mathbf{r},\mathbf{v},t\right)-h\left(\mathbf{r},\mathbf{v}_2,t\right)\right)$$