PHY 341/641 Thermodynamics and Statistical Mechanics
MWF: Online at 12 PM & FTF at 2 PM

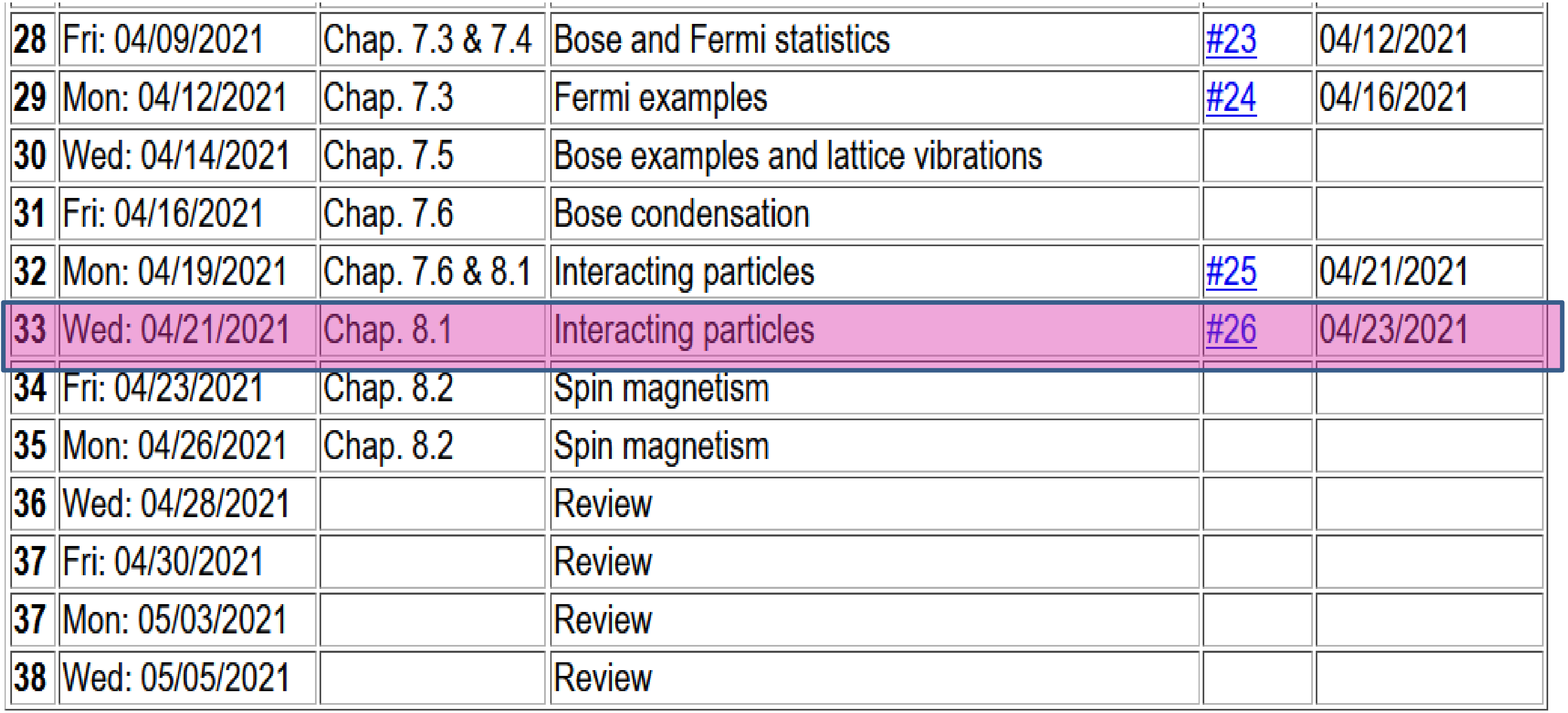
Record!!!

Discussion for Lecture 33:

Treatment of particle interactions in statistical mechanics

Reading: Sections 8.1

1. **Treatment and effects of interparticle interactions in statistical mechanics**
2. **Corrections to the ideal gas law; virial coefficient**



28	Fri: 04/09/2021	Chap. 7.3 & 7.4	Bose and Fermi statistics	#23	04/12/2021
29	Mon: 04/12/2021	Chap. 7.3	Fermi examples	#24	04/16/2021
30	Wed: 04/14/2021	Chap. 7.5	Bose examples and lattice vibrations		
31	Fri: 04/16/2021	Chap. 7.6	Bose condensation		
32	Mon: 04/19/2021	Chap. 7.6 & 8.1	Interacting particles	#25	04/21/2021
33	Wed: 04/21/2021	Chap. 8.1	Interacting particles	#26	04/23/2021
34	Fri: 04/23/2021	Chap. 8.2	Spin magnetism		
35	Mon: 04/26/2021	Chap. 8.2	Spin magnetism		
36	Wed: 04/28/2021		Review		
37	Fri: 04/30/2021		Review		
37	Mon: 05/03/2021		Review		
38	Wed: 05/05/2021		Review		

PHY 341/641 -- Assignment #26

April 21, 2021

Complete reading Section 8.1 in **Schroeder** .

Choose some appropriate values for the Lennard-Jones potential form for your favorite atom (r_0 and Φ_0).

1. For three different temperatures *T* evaluate the second virial coefficient *B(T)* using Maple, Mathematica, or other software of your choice.
2. Qualitatively, what controls the sign of the second virial coefficient?

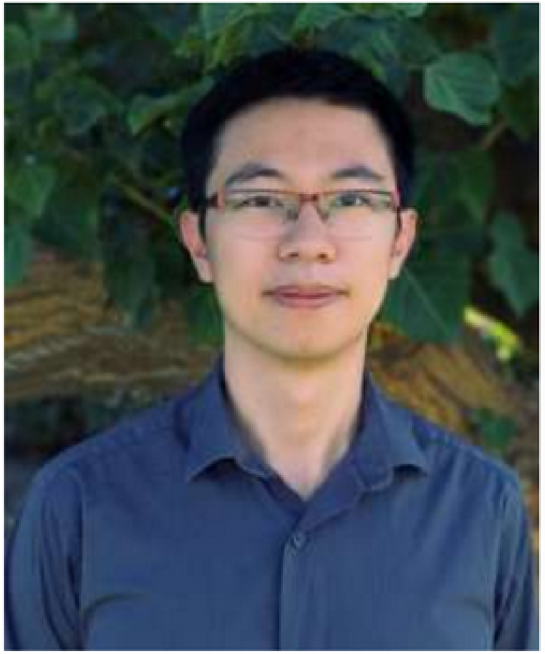
PHYSICS COLLOQUIUM

4 PM

THURSDAY
•
APRIL 22, 2021

“Quantum Computing with Superconducting Qubits”

Quantum computers promise to perform certain computational tasks exponentially faster than classical processors. However, achieving these speed-ups requires sufficiently low error rates in the quantum processor. In this talk, I will discuss the development of a programmable quantum processor named Sycamore, which consists of 53 superconducting qubits with state of the art operational fidelities. We benchmark the performance of Sycamore on randomly generated quantum circuits which are significantly more complex than any previous quantum computation. We also show



Dr. Jimmy Chen
Research Scientist
Google AI Quantum

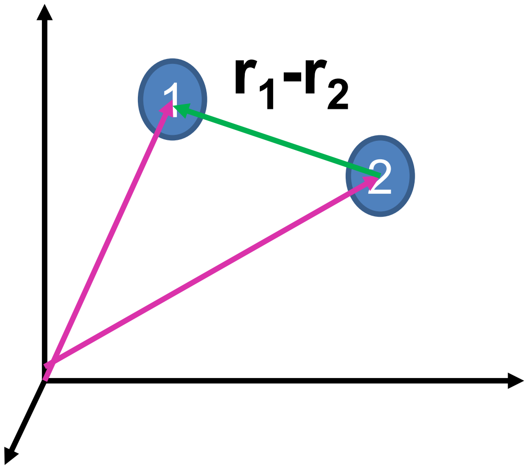
Up to now, we have focused on systems that can be well described as independent (non-interacting) particles. More realistically, particles do interact. Typically this interaction can be described in terms an interacting potential energy term. As an example, we will consider a gas of N monoatomic atoms of mass m treated using classical mechanics .

The classical Hamiltonian of the system has kinetic energy

and potential energy contributions: $$\mathcal{H}=\sum_{i=1}^{N}\frac{\left|\mathbf{p}_i\right|^2}{2m}+\Phi(\mathbf{r}_1,\mathbf{r}_2..)$$

We have been ignoring this term

Some typical potential interactions



Coulomb interaction

$$\Phi(|\mathbf{r}_1-\mathbf{r}_2|)=\frac{q^2}{4\pi\epsilon_0}\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}$$

Lennard-Jones interaction

$$\Phi(|\mathbf{r}_1-\mathbf{r}_2|)=\Phi_0\left(\left(\frac{r_0}{|\mathbf{r}_1-\mathbf{r}_2|}\right)^{12}-2\left(\frac{r_0}{|\mathbf{r}_1-\mathbf{r}_2|}\right)^{6}\right)$$

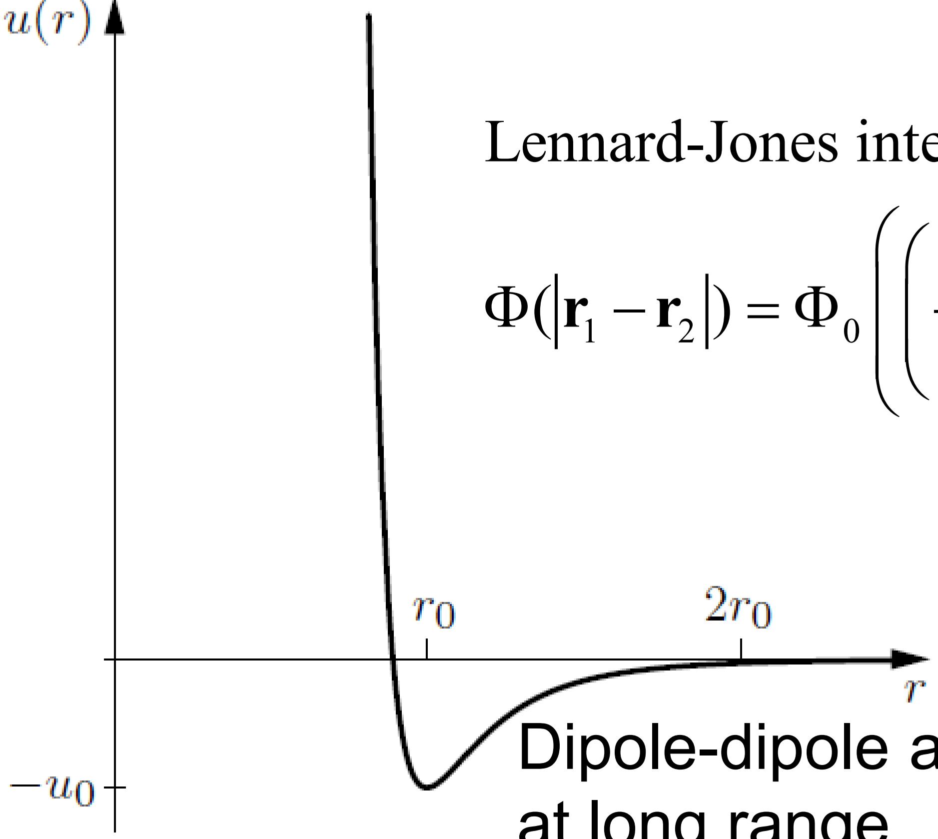
Born-Mayer potential

$$\Phi(|\mathbf{r}_1-\mathbf{r}_2|)=\Phi_0 e^{-\lambda|\mathbf{r}_1-\mathbf{r}_2|}+\frac{q^2}{4\pi\epsilon_0}\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}$$

In practice, potential interactions can involve more than 2 particles and can be angularly dependent.

The Lennard-Jones pair potential does a good job of describing the interaction between rare gas atoms.

Repulsive interaction
at short range



Lennard-Jones interaction

$$\Phi(|\mathbf{r}_1-\mathbf{r}_2|)=\Phi_0\left(\left(\frac{r_0}{|\mathbf{r}_1-\mathbf{r}_2|}\right)^{12}-2\left(\frac{r_0}{|\mathbf{r}_1-\mathbf{r}_2|}\right)^{6}\right)$$

Dipole-dipole attraction
at long range

Measured Lennard-Jones parameters for some rare gas atoms (Ref. Ashcroft and Mermin, Solid State Physics)

	Ne	Ar	Kr	Xe
U_0 (eV)	0.0031	0.0104	0.0140	0.0200
r_0 (Angstroms)	3.08	3.82	4.10	4.47

$$\Phi(\mathbf{r}_1, \mathbf{r}_2 \ldots) \approx \sum_{pairs\ (ij)} \phi_{pair}\left(\left|\mathbf{r}_i - \mathbf{r}_j\right|\right)$$

Classical canonical partition function for gas of particles of mass m in the presence of an interaction potential

$$Z(T,V,N)=\frac{1}{N!h^{3N}}\int d^3r_1 d^3r_2..d^3r_N d^3p_1 d^3p_2..d^3p_N e^{-\beta\mathcal{H}}$$

$$\text{where}\quad \mathcal{H}=\sum_{i=1}^{N}\frac{|\mathbf{p}_i|^2}{2m}+\Phi(\mathbf{r}_1,\mathbf{r}_2..)\equiv\mathcal{H}_{kin}+\Phi(\mathbf{r}_1,\mathbf{r}_2..)$$

$$Z(T,V,N)=Z_{kin}(T,V,N)Z_{pot}(T,V,N)$$

$$Z_{kin}(T,V,N)\equiv\frac{V^N}{N!h^{3N}}\int d^3p_1 d^3p_2..d^3p_N e^{-\beta\mathcal{H}_{kin}}$$

$$=\frac{V^N}{N!}\left(\frac{2\pi mkT}{h^2}\right)^{3N/2}$$

$$Z_{pot}(T,V,N)\equiv\frac{1}{V^N}\int d^3r_1 d^3r_2..d^3r_N e^{-\beta\Phi(\mathbf{r}_1,\mathbf{r}_2..)}$$

Evaluation of the potential contributions --

$$Z_{pot}(T,V,N) \equiv \frac{1}{V^N} \int d^3r_1 d^3r_2 .. d^3r_N e^{-\beta\Phi(\mathbf{r}_1,\mathbf{r}_2..)}$$

$$\Phi(\mathbf{r}_1,\mathbf{r}_2...) \approx \sum_{pairs\ (ij)} \phi_{pair}(|\mathbf{r}_i - \mathbf{r}_j|)$$

$$Z_{pot}(T,V,N) \approx \frac{1}{V^N} \int d^3r_1 d^3r_2 .. d^3r_N \prod_{pairs(ij)} e^{-\beta\phi_{pair}(|\mathbf{r}_i - \mathbf{r}_j|)}$$

Suppose that $e^{-\beta\phi_{pair}(|\mathbf{r}_i - \mathbf{r}_j|)} \equiv 1 + f_{ij}$ $\quad f_{ij} = e^{-\beta\phi_{pair}(|\mathbf{r}_i - \mathbf{r}_j|)} - 1$

Then $\prod_{pairs(ij)} e^{-\beta\phi_{pair}(|\mathbf{r}_i - \mathbf{r}_j|)} = (1+f_{12})(1+f_{13})...(1+f_{23})...(1+f_{N-1N})$

$$=1+\sum_{pairs(ij)} f_{ij} + \sum_{pairs(ij,kl)} f_{ij}f_{kl} + ...$$

Comment --

$$f_{ij} = e^{-\beta\phi_{pair}(|\mathbf{r}_i - \mathbf{r}_j|)} - 1 \quad \rightarrow f(r) = e^{-\beta\phi_{pair}(r)} - 1$$

For $\phi_{pair}(r \rightarrow \infty) \approx 0, \qquad f(r \rightarrow \infty) \approx 0$

Evaluation of potential terms continued --

$$Z_{pot}(T,V,N) \approx \frac{1}{V^N}\int d^3r_1 d^3r_2 .. d^3r_N \prod_{pairs(ij)} e^{-\beta\phi_{pair}(|\mathbf{r}_i-\mathbf{r}_j|)}$$

$$= Z^0_{pot}(T,V,N) + Z^{pairs}_{pot}(T,V,N) + Z^{double\ pairs}_{pot}(T,V,N) + ...$$

$$Z^0_{pot}(T,V,N) = \frac{1}{V^N}\int d^3r_1 d^3r_2 .. d^3r_N = 1$$

$$Z^{pairs}_{pot}(T,V,N) = \frac{1}{V^N}\int d^3r_1 d^3r_2 .. d^3r_N \sum_{pairs(ij)} f_{ij} = \frac{1}{2}\frac{N(N-1)}{V^2}\int d^3r_1 d^3r_2 f_{12}$$

Some details --

For N particles, the number of pairs is $\dfrac{N(N-1)}{2}$

Evaluation of the pair contribution --

$$X_{pair} \equiv \int d^3r_1 d^3r_2 f_{12} = \int d^3r_1 d^3r_{12} \left(e^{-\beta\phi_{pair}(r_{12})} - 1\right)$$

$$= 4\pi V \int_0^\infty r^2 dr \left(e^{-\beta\phi_{pair}(r)} - 1\right)$$

Lennard-Jones interaction: $\phi_{pair}(|\mathbf{r}_1 - \mathbf{r}_2|) = \Phi_0 \left(\left(\frac{r_0}{|\mathbf{r}_1 - \mathbf{r}_2|} \right)^{12} - 2 \left(\frac{r_0}{|\mathbf{r}_1 - \mathbf{r}_2|} \right)^6 \right)$

$$X_{pair} = 4\pi V r_0^3 \int_0^\infty u^2 du \left(e^{-b\left(u^{-12} - 2u^{-6}\right)} - 1 \right) \quad \text{where } b \equiv \frac{\Phi_0}{kT}$$

$$\equiv 4\pi V r_0^3 I_{pair}(\Phi_0 / kT)$$

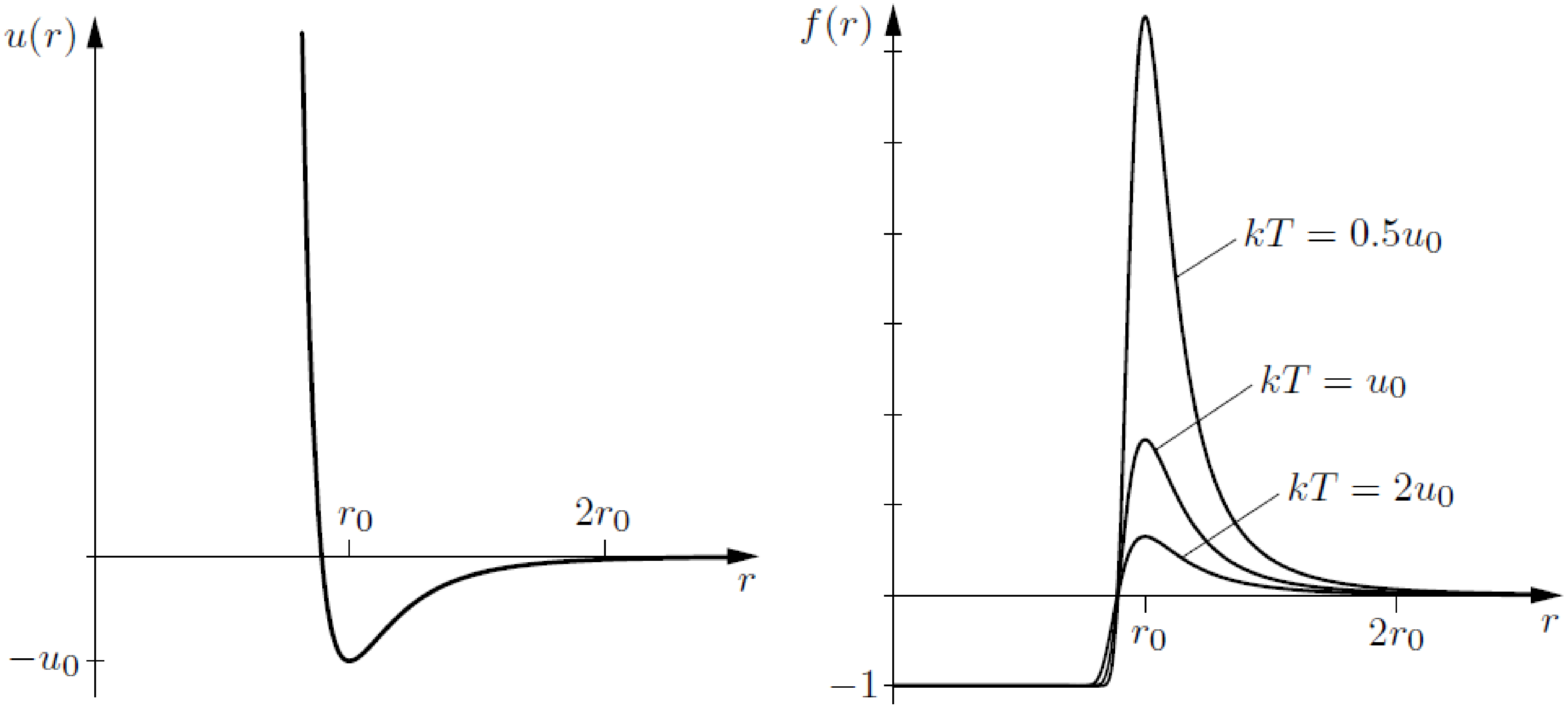
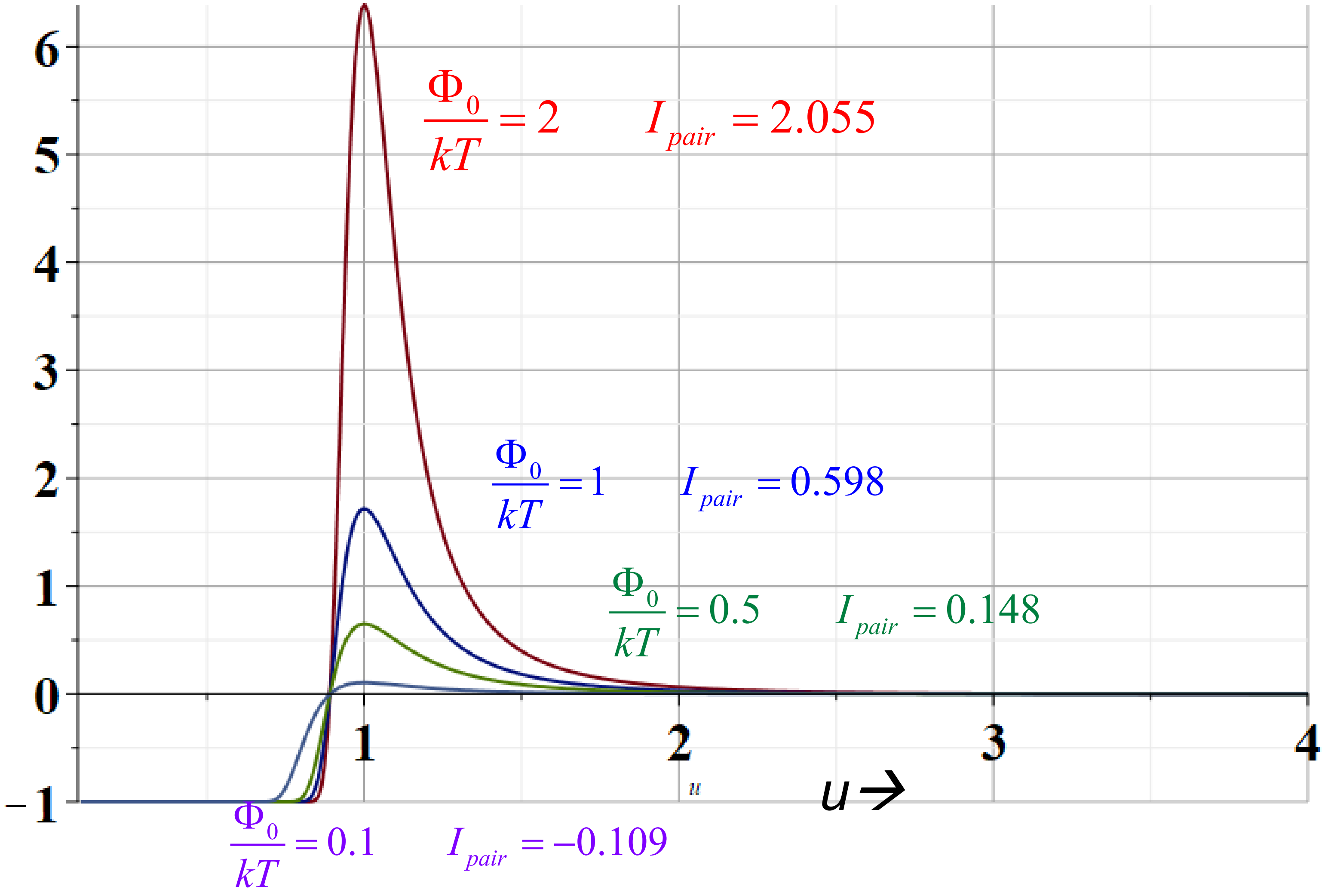
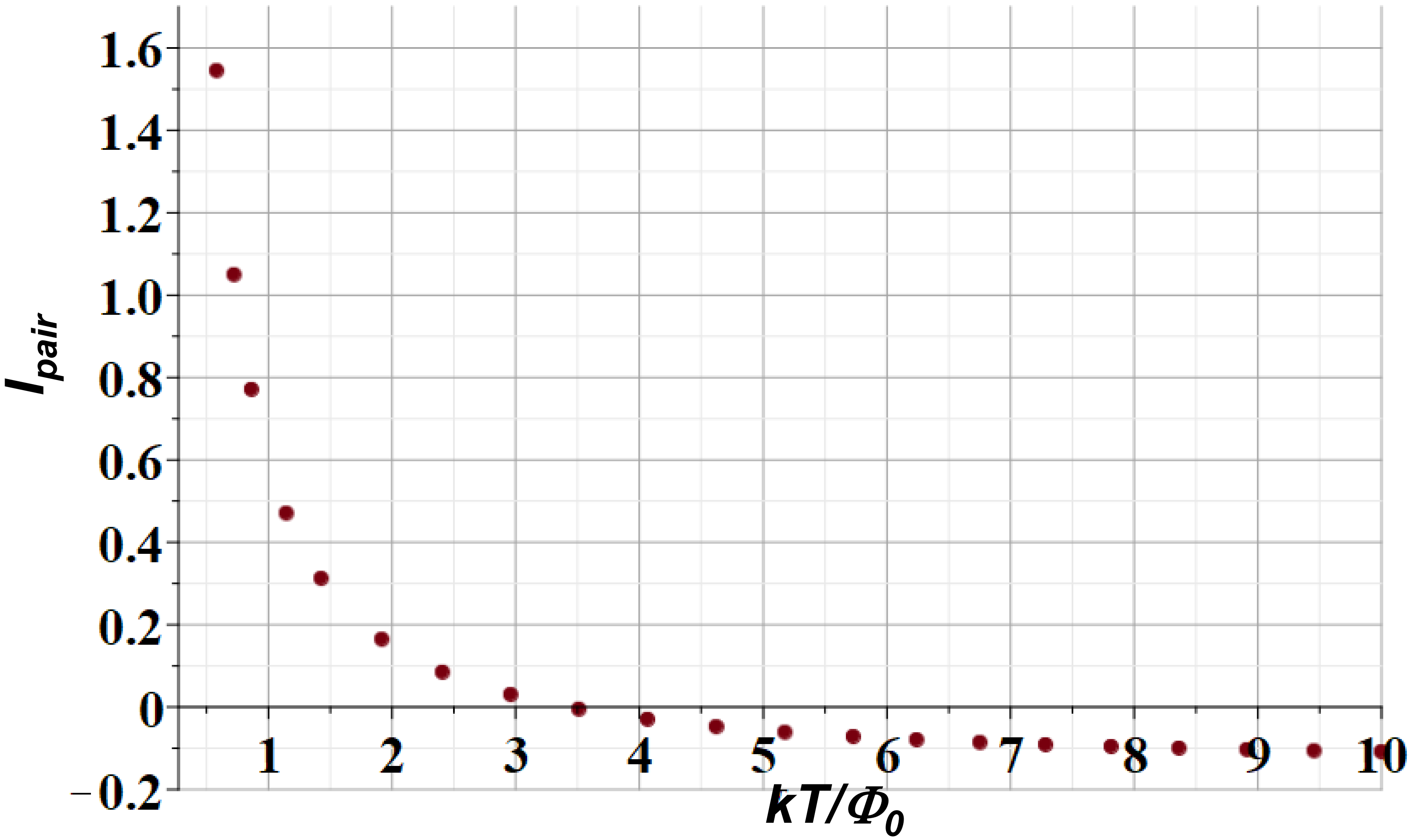


Figure 8.1. Left: The Lennard-Jones intermolecular potential function, with a strong repulsive region at small distances and a weak attractive region at somewhat larger distances. Right: The corresponding Mayer f-function, for three different temperatures. Copyright ©2000, Addison-Wesley.

Plot of $e^{-b\left(u^{-12}-2u^{-6}\right)}-1$ for $b \equiv \frac{\Phi_0}{kT}$




I_{pair}
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
−0.2
1
2
3
4
5
6
7
8
9
10
kT/Φ_0

Evaluating the partition function for this case

$$Z(T,V,N) = Z_{kin}(T,V,N)Z_{pot}(T,V,N)$$

$$Z_{kin}(T,V,N) \equiv \frac{V^N}{N!h^{3N}} \int d^3p_1 d^3p_2 .. d^3p_N e^{-\beta \mathcal{H}_{kin}}$$

$$= \frac{V^N}{N!} \left(\frac{2\pi mkT}{h^2} \right)^{3/2}$$

$$Z_{pot}(T,V,N) \equiv \frac{1}{V^N} \int d^3r_1 d^3r_2 .. d^3r_N e^{-\beta \Phi(\mathbf{r}_1, \mathbf{r}_2 ..)}$$

$$\approx Z^0_{pot}(T,V,N) + Z^{pairs}_{pot}(T,V,N)$$

$$Z(T,V,N) = Z_{kin}(T,V,N)Z_{pot}(T,V,N)$$

$$\approx \frac{V^N}{N!}\left(\frac{2\pi mkT}{h^2}\right)^{3N/2}\left(1+\frac{4\pi r_0^3 N(N-1)}{2V} I_{pair}(\Phi_0/kT)\right)$$

$$F(T,V,N) = -NkT\left(\ln\left(\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{3N/2}\right)+1\right) - kT\ln\left(1+\frac{4\pi r_0^3 N(N-1)}{2V} I_{pair}(\Phi_0/kT)\right)$$

$$\approx -NkT\left(\ln\left(\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{3N/2}\right)+1\right) - kT\left(\frac{4\pi r_0^3 N(N-1)}{2V} I_{pair}(\Phi_0/kT)\right)$$

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} \approx \frac{NkT}{V} - \frac{N^2kT}{V^2}\left(2\pi r_0^3 I_{pair}(\Phi_0/kT)\right)$$

Note that $\ln(1+x) = x - \frac{1}{2}x^2 .....$

Virial expansion up to second order

$$P = \frac{NkT}{V}\left(1 + \frac{B(T)}{V/N}\right)$$

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} \approx \frac{NkT}{V} - \frac{N^2kT}{V^2}\left(2\pi r_0^3 I_{pair}(\Phi_0/kT)\right)$$

$\Rightarrow B(T) = -2\pi r_0^3 I_{pair}(\Phi_0/kT)$ for the Lennard-Jones case

More generally --

$$B(T) = -2\pi\int_0^\infty r^2 dr\left(e^{-\beta\phi_{pair}(r)} - 1\right)$$

Plot of second virial coefficients from Schroeder --

$$\Rightarrow B(T) = -2\pi r_0^3 I_{pair}(\Phi_0 / kT) \quad \text{for the Lennard-Jones case}$$

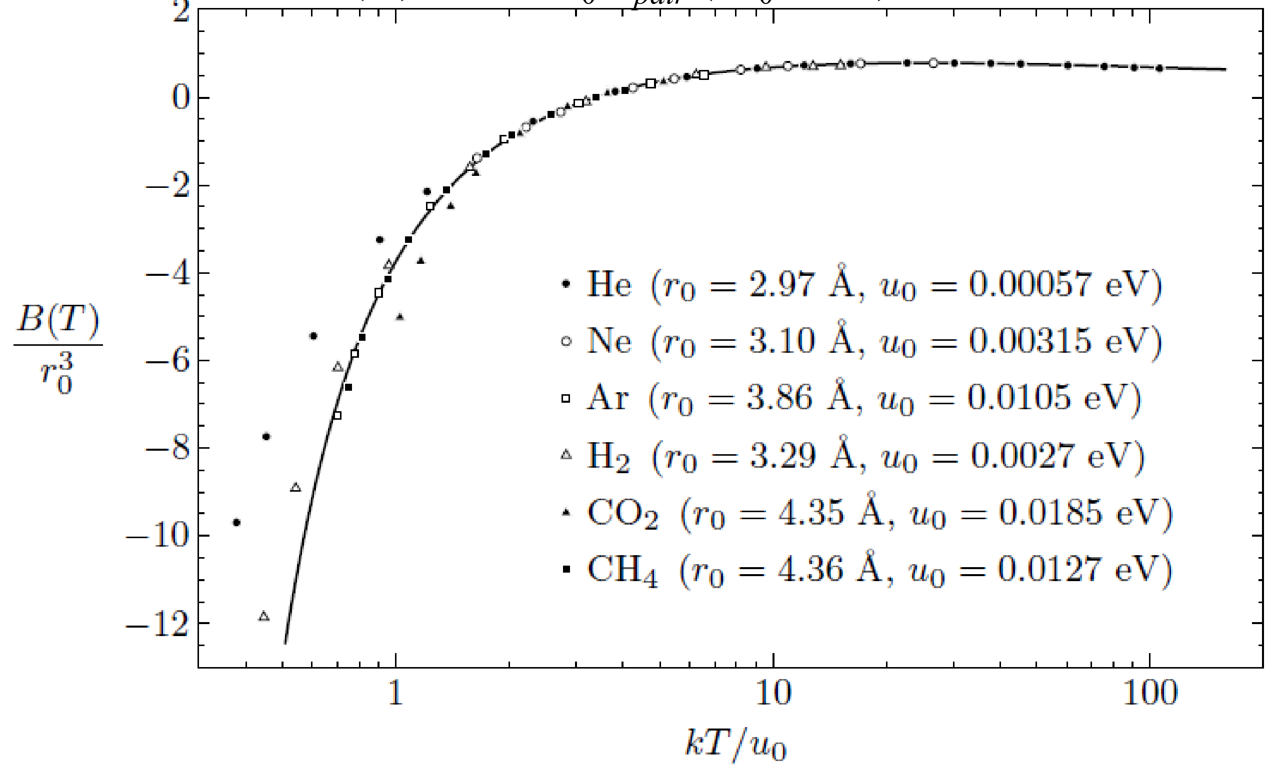


Figure 8.2. Measurements of the second virial coefficients of selected gases, compared to the prediction of equation 8.36 with $u(r)$ given by the Lennard-Jones function. Note that the horizontal axis is logarithmic. The constants r_0 and u_0 have been chosen separately for each gas to give the best fit. For carbon dioxide, the poor fit is due to the asymmetric shape of the molecules. For hydrogen and helium, the discrepancies at low temperatures are due to quantum effects. Data from J. H. Dymond and E. B. Smith, *The Virial Coefficients of Pure Gases and Mixtures: A Critical Compilation* (Oxford University Press, Oxford, 1980).

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