Answer all problems, but note that the first parts of each problem are easier than its last parts. Therefore, make sure to proceed to the next problem when you get stuck.

You may find the following information helpful:

Physical Constants

Electron mass	$m_e \approx 9.1 \times 10^{-31}$kg	Proton mass	$m_p \approx 1.7 \times 10^{-27}$kg
Electron Charge	$e \approx 1.6 \times 10^{-19}$C	Planck's constant/2π	$\hbar \approx 1.1 \times 10^{-34}$Js
Speed of light	$c \approx 3.0 \times 10^8$ms^{-1}	Stefan's constant	$\sigma \approx 5.7 \times 10^{-8}Wm^{-2}\,^{\circ}$K^{-4}
Boltzmann's constant	$k_B \approx 1.4 \times 10^{-23} JK^{-1}$	Avogadro's number	$N_0 \approx 6.0 \times 10^{23}$mol^{-1}
Gravitational constant	$G \approx 6.7 \times 10^{-11}$Nm^{2}kg^{-2}		

Conversion Factors

$$1atm \equiv 1.0 \times 10^5 Nm^{-2} \qquad\qquad 1\mathring{A} \equiv 10^{-10}m \qquad\qquad 1eV \equiv 1.1 \times 10^{4}\,^{\circ}K$$

Thermodynamics

$$dE = TdS + dW \qquad\qquad \text{For a gas: } dW = -PdV \qquad\qquad \text{For a film: } dW = \sigma dA$$

Mathematical Formulas

$$\lim_{x\to 0} \ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} + \mathcal{O}\left(x^4\right) \qquad\qquad \lim_{x\to\infty} \ln(1+x) = \ln x + \frac{1}{x} + \mathcal{O}\left(\frac{1}{x^2}\right)$$

$$\lim_{x\to\infty} \coth x = 1 + 2e^{-2x} + \mathcal{O}\left(e^{-4x}\right) \qquad\qquad \lim_{x\to 0} \coth x = \frac{1}{x} + \frac{x}{3} + \mathcal{O}\left(x^2\right)$$

$$\int_0^\infty dx\, x^n\, e^{-\alpha x} = \frac{n!}{\alpha^{n+1}} \qquad\qquad \left(\frac{1}{2}\right)! = \frac{\sqrt{\pi}}{2}$$

$$\int_{-\infty}^\infty dx \exp\left[-ikx - \frac{x^2}{2\sigma^2}\right] = \sqrt{2\pi\sigma^2}\exp\left[-\frac{\sigma^2 k^2}{2}\right] \qquad\qquad \lim_{N\to\infty} \ln N! = N\ln N - N$$

$$\left\langle e^{-ikx}\right\rangle = \sum_{n=1}^\infty \frac{(-ik)^n}{n!}\left\langle x^n\right\rangle \qquad\qquad \ln\left\langle e^{-ikx}\right\rangle = \sum_{n=1}^\infty \frac{(-ik)^n}{n!}\left\langle x^n\right\rangle_c$$

$$f_m^\eta(z) = \frac{1}{(m-1)!}\int_0^\infty dx\frac{x^{m-1}}{z^{-1}e^x - \eta} = \sum_{\alpha=1}^\infty \eta^{\alpha+1}\frac{z^\alpha}{\alpha^m} \qquad\qquad \frac{df_m^\eta}{dz} = \frac{1}{z}f_{m-1}^\eta$$

$$\zeta_m \equiv f_m^+(1) \qquad \zeta_{3/2} \approx 2.612 \qquad \zeta_2 = \frac{\pi^2}{6} \qquad \zeta_{5/2} \approx 1.341 \qquad \zeta_3 \approx 1.202 \qquad \zeta_4 = \frac{\pi^4}{90}$$

$$\lim_{z\to\infty} f_m^-(z) = \frac{(\ln z)^m}{m!}\left[1 + \frac{\pi^2}{6}m(m-1)(\ln z)^{-2} + \cdots\right] \quad f_m^-(1) = \left(1 - 2^{1-m}\right)\zeta_m$$

1. *Graphene* is a single sheet of carbon atoms bonded into a *two dimensional* hexagonal lattice. It can be obtained by exfoliation (repeated peeling) of graphite. The band structure of graphene is such that the single particles excitations behave as relativistic Dirac *fermions*, with a spectrum that at low energies can be approximated by

$$\mathcal{E}_\pm(\vec{k}) = \pm \hbar v \left| \vec{k} \right| \quad .$$

There is spin degeneracy of $g = 2$, and $v \approx 10^6 \text{ms}^{-1}$. Recent experiments on unusual transport properties of graphene were reported in *Nature* **438**, 197 (2005). In this problem, you shall calculate the heat capacity of this material.

(a) If at zero temperature all negative energy states are occupied and all positive energy ones are empty, find the chemical potential $\mu(T)$.

• According to Fermi statistics, the probability of occupation of a state of of energy $\mathcal{E}$ is

$$p\left[n(\mathcal{E})\right] = \frac{e^{\beta(\mu-\mathcal{E})n}}{1 + e^{\beta(\mu-\mathcal{E})}}, \qquad \text{for} \quad n = 0, 1.$$

For a state of energy $\mu + \delta$,

$$p\left[n(\mu+\delta)\right] = \frac{e^{\beta\delta n}}{1 + e^{\beta\delta}}, \quad \Longrightarrow \quad p\left[n(\mu+\delta) = 1\right] = \frac{e^{\beta\delta}}{1 + e^{\beta\delta}} = \frac{1}{1 + e^{-\beta\delta}}.$$

Similarly, for a state of energy $\mu - \delta$,

$$p\left[n(\mu-\delta)\right] = \frac{e^{-\beta\delta n}}{1 + e^{-\beta\delta}}, \quad \Longrightarrow \quad p\left[n(\mu-\delta) = 0\right] = \frac{1}{1 + e^{-\beta\delta}} = p\left[n(\mu+\delta) = 1\right],$$

i.e. the probability of finding an occupied state of energy $\mu + \delta$ is the same as that of finding an unoccupied state of energy $\mu - \delta$.

At zero temperature all negative energy Dirac states are occupied and all positive energy ones are empty, i.e. $\mu(T = 0) = 0$. The above result implies that for $\mu = 0$, $\langle n(\mathcal{E}) \rangle + \langle n - \mathcal{E}) \rangle$ is unchanged for all temperatures; any particle leaving an occupied negative energy state goes to the corresponding unoccupied positive energy state. Adding up all such energies, we conclude that the total particle number is unchanged if μ stays at zero. Thus, the particle–hole symmetry enforces $\mu(T) = 0$.

(b) Show that the mean excitation energy of this system at finite temperature satisfies

$$E(T) - E(0) = 4A \int \frac{d^2\vec{k}}{(2\pi)^2} \frac{\mathcal{E}_+(\vec{k})}{\exp\left(\beta\mathcal{E}_+(\vec{k})\right) + 1} \quad .$$

• Using the label +(-) for the positive (energy) states, the excitation energy is calculated as

$$E(T) - E(0) = \sum_{k,s_z} \left[\langle n_+(k) \rangle \mathcal{E}_+(k) + (1 - \langle n_-(k) \rangle) \mathcal{E}_-(k) \right]$$

$$= 2\sum_k 2 \langle n_+(k) \rangle \mathcal{E}_+(k) = 4A \int \frac{d^2\vec{k}}{(2\pi)^2} \frac{\mathcal{E}_+(\vec{k})}{\exp\left(\beta\mathcal{E}_+(\vec{k})\right) + 1}.$$

(c) Give a closed form answer for the excitation energy by evaluating the above integral.

• For $\mathcal{E}_+(k) = \hbar v|k|$, and

$$E(T) - E(0) = 4A \int_0^\infty \frac{2\pi k dk}{4\pi^2} \frac{\hbar v k}{e^{\beta \hbar v k} + 1} = \quad (\text{set } \beta\hbar ck = x)$$

$$= \frac{2A}{\pi} k_B T \left(\frac{k_B T}{\hbar v}\right)^2 \int_0^\infty dx \frac{x^2}{e^x + 1}$$

$$= \frac{3\zeta_3}{\pi} A k_B T \left(\frac{k_B T}{\hbar v}\right)^2.$$

For the final expression, we have noted that the needed integral is $2! f_3^-(1)$, and used $f_3^-(1) = 3\zeta_3/4$.

$$E(T) - E(0) = A \int \frac{d^2\vec{k}}{(2\pi)^2} \frac{\mathcal{E}_+(\vec{k})}{\exp\left(\beta\mathcal{E}_+(\vec{k})\right) - 1} \quad .$$

(d) Calculate the heat capacity, C_V, of such massless Dirac particles.

• The heat capacity can now be evaluated as

$$C_V = \left.\frac{\partial E}{\partial T}\right|_V = \frac{9\zeta_3}{\pi} A k_B \left(\frac{k_B T}{\hbar v}\right)^2.$$

(e) Explain qualitatively the contribution of phonons (lattice vibrations) to the heat capacity of graphene. The typical sound velocity in graphite is of the order of $2\times10^4 \text{ms}^{-1}$. Is the low temperature heat capacity of graphene controlled by phonon or electron contributions?

• The single particle excitations for phonons also have a linear spectrum, with $\mathcal{E}_p = \hbar v_p |k|$ and correspond to $\mu = 0$. Thus qualitatively they give the same type of contribution to energy and heat capacity. The difference is only in numerical pre-factors. The precise contribution from a single phonon branch is given by

$$E_p(T) - E_p(0) = A \int_0^\infty \frac{2\pi k dk}{4\pi^2} \frac{\hbar v_p k}{e^{\beta \hbar v_p k} - 1} = \qquad (\text{set } \beta \hbar c k = x)$$

$$= \frac{A}{2\pi} k_B T \left(\frac{k_B T}{\hbar v_p} \right)^2 \int_0^\infty dx \frac{x^2}{e^x - 1}$$

$$= \frac{\zeta_3}{\pi} A k_B T \left(\frac{k_B T}{\hbar v_p} \right)^2, \quad C_{V,p} = \frac{3\zeta_3}{\pi} A k_B \left(\frac{k_B T}{\hbar v_p} \right)^2.$$

We see that the ratio of electron to phonon heat capacities is proportional to $(v_p/v)^2$. Since the speed of Dirac fermions is considerably larger than that of phonons, their contribution to heat capacity of graphene is negligible.

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2. *Quantum Coulomb gas:* Consider a *quantum* system of N positive, and N negative charged relativistic particles in box of volume $V = L^3$. The Hamiltonian is

$$\mathcal{H} = \sum_{i=1}^{2N} c|\vec{p}_i| + \sum_{i<j}^{2N} \frac{e_i e_j}{|\vec{r}_i - \vec{r}_j|} \quad,$$

where $e_i = +e_0$ for $i = 1, \cdots N$, and $e_i = -e_0$ for $i = N+1, \cdots 2N$, denote the charges of the particles; $\{\vec{r}_i\}$ and $\{\vec{p}_i\}$ their coordinates and momenta respectively. While this is too complicated a system to solve, we can nonetheless obtain some exact results.

(a) Write down the Schrödinger equation for the eigenvalues $\varepsilon_n(L)$, and (in coordinate space) eigenfunctions $\Psi_n(\{\vec{r}_i\})$. State the constraints imposed on $\Psi_n(\{\vec{r}_i\})$ if the particles are bosons or fermions?

• In the coordinate representation $\vec{p}_i$ is replaced by $-i\hbar\nabla_i$, leading to the Schrödinger equation

$$\left[\sum_{i=1}^{2N} c| - i\hbar\nabla_i| + \sum_{i<j}^{2N} \frac{e_i e_j}{|\vec{r}_i - \vec{r}_j|} \right] \Psi_n(\{\vec{r}_i\}) = \varepsilon_n(L)\Psi_n(\{\vec{r}_i\}).$$

There are N identical particles of charge $+e_0$, and N identical particles of charge $-e_0$. We can examine the effect of permutation operators P_+ and P_- on these two sets. The

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symmetry constraints can be written compactly as

$$P_+ P_- \Psi_n(\{\vec{r}_i\}) = \eta_+^{P_+} \cdot \eta_-^{P_-} \Psi_n(\{\vec{r}_i\}),$$

where $\eta = +1$ for bosons, $\eta = -1$ for fermions, and $(-1)^P$ denotes the parity of the permutation. Note that there is no constraint associated with exchange of particles with opposite charge.

(b) By a change of scale $\vec{r}_i' = \vec{r}_i/L$, show that the eigenvalues satisfy a scaling relation $\varepsilon_n(L) = \varepsilon_n(1)/L$.

• After the change of scale $\vec{r}_i' = \vec{r}_i/L$ (and corresponding change in the derivative $\nabla_i' = L\nabla_i$), the above Schrödinger equation becomes

$$\left[\sum_{i=1}^{2N} c \left| -i\hbar \frac{\nabla_i'}{L} \right| + \sum_{i<j}^{2N} \frac{e_i e_j}{L \, |\vec{r}_i' - \vec{r}_j'|} \right] \Psi_n \left(\left\{ \frac{\vec{r}_i'}{L} \right\} \right) = \varepsilon_n(L) \Psi_n \left(\left\{ \frac{\vec{r}_i'}{L} \right\} \right).$$

The coordinates in the above equation are confined to a box of unit size. We can regard it as the Schrödinger equation in such a box, with wave-functions $\Psi_n'(\{\vec{r}_i\}) = \Psi_n(\{\vec{r}_i'/L\})$. The corresponding eigenvalues are $\varepsilon_n(1) = L\varepsilon_n(L)$ (obtained after multiplying both sides of the above equation by L We thus obtain the scaling relation

$$\varepsilon_n(L) = \frac{\varepsilon_n(1)}{L}.$$

(c) Using the formal expression for the partition function $Z(N, V, T)$, in terms of the eigenvalues $\{\varepsilon_n(L)\}$, show that Z does not depend on T and V separately, but only on a specific scaling combination of them.

• The formal expression for the partition function is

$$Z(N, V, T) = \text{tr}\left(e^{-\beta \mathcal{H}}\right) = \sum_n \exp\left(-\frac{\varepsilon_n(L)}{k_B T}\right)$$
$$= \sum_n \exp\left(-\frac{\varepsilon_n(1)}{k_B T L}\right),$$

where we have used the scaling form of the energy levels. Clearly, in the above sum T and L always occur in the combination TL. Since $V = L^3$, the appropriate scaling variable is VT^3, and

$$Z(N, V, T) = \mathcal{Z}(N, VT^3).$$

(d) Relate the energy E, and pressure P of the gas to variations of the partition function. Prove the exact result $E = 3PV$.

- The average energy in the canonical ensemble is given by

$$E = -\frac{\partial \ln Z}{\partial \beta} = k_B T^2 \frac{\partial \ln Z}{\partial T} = k_B T^2 (3VT^2) \frac{\partial \ln \mathcal{Z}}{\partial (VT^3)} = 3k_B VT^4 \frac{\partial \ln \mathcal{Z}}{\partial (VT^3)}.$$

The free energy is $F = -k_B T \ln Z$, and its variations are $dF = -SdT - PdV + \mu dN$. Hence the gas pressure is given by

$$P = -\frac{\partial F}{\partial V} = k_B T \frac{\partial \ln Z}{\partial V} = k_B T^4 \frac{\partial \ln \mathcal{Z}}{\partial (VT^3)}.$$

The ratio of the above expressions gives the exact identity $E = 3PV$.

(e) The Coulomb interaction between charges in in d-dimensional space falls off with separation as $e_i e_j / |\vec{r}_i - \vec{r}_j|^{d-2}$. (In $d = 2$ there is a logarithmic interaction.) In what dimension d can you construct an exact relation between E and P for *non-relativistic* particles (kinetic energy $\sum_i \vec{p}_i^2 / 2m$)? What is the corresponding exact relation between energy and pressure?

- The above exact result is a consequence of the simple scaling law relating the energy eigenvalues $\varepsilon_n(L)$ to the system size. We could obtain the scaling form in part (b) since the kinetic and potential energies scaled in the same way. The kinetic energy for *non-relativistic* particles $\sum_i \vec{p}_i^2 / 2m = -\sum_i \hbar^2 \nabla_i^2 / 2m$, scales as $1/L^2$ under the change of scale $\vec{r}_i' = \vec{r}_i / L$, while the interaction energy $\sum_{i<j}^{2N} e_i e_j / |\vec{r}_i - \vec{r}_j|^{d-2}$ in d space dimensions scales as $1/L^{d-2}$. The two forms will scale the same way in $d = 4$ dimensions, leading to

$$\varepsilon_n(L) = \frac{\varepsilon_n(1)}{L^2}.$$

The partition function now has the scaling form

$$Z(N, V = L^4, T) = \mathcal{Z}\left(N, (TL^2)^2\right) = \mathcal{Z}\left(N, VT^2\right).$$

Following steps in the previous part, we obtain the exact relationship $E = 2PV$.

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(f) Why are the above 'exact' scaling laws not expected to hold in dense (liquid or solid) Coulomb mixtures?

• The scaling results were obtained based on the assumption of the existence of a single scaling length L, relevant to the statistical mechanics of the problem. This is a good approximation in a gas phase. In a dense (liquid or solid) phase, the short-range repulsion between particles is expected to be important, and the particle size a is another relevant length scale which will enter in the solution to the Schrödinger equation, and invalidate the scaling results.

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3. *Non-interacting Fermions:* Consider a grand canonical ensemble of non-interacting *fermions* with chemical potential μ. The one–particle states are labelled by a wavevector $\vec{k}$, and have energies $\mathcal{E}(\vec{k})$.

(a) What is the joint probability $P(\{n_{\vec{k}}\})$, of finding a set of occupation numbers $\{n_{\vec{k}}\}$, of the one–particle states?

• In the grand canonical ensemble with chemical potential μ, the joint probability of finding a set of occupation numbers $\{n_{\vec{k}}\}$, for one–particle states of energies $\mathcal{E}(\vec{k})$ is given by the Fermi distribution

$$P(\{n_{\vec{k}}\}) = \prod_{\vec{k}} \frac{\exp\left[\beta(\mu - \mathcal{E}(\vec{k}))n_{\vec{k}}\right]}{1 + \exp\left[\beta(\mu - \mathcal{E}(\vec{k}))\right]}, \qquad \text{where} \quad n_{\vec{k}} = 0 \text{ or } 1, \quad \text{for each } \vec{k}.$$

(b) Express your answer to part (a) in terms of the average occupation numbers $\left\{\langle n_{\vec{k}}\rangle_-\right\}$.

• The average occupation numbers are given by

$$\langle n_{\vec{k}}\rangle_- = \frac{\exp\left[\beta(\mu - \mathcal{E}(\vec{k}))\right]}{1 + \exp\left[\beta(\mu - \mathcal{E}(\vec{k}))\right]},$$

from which we obtain

$$\exp\left[\beta(\mu - \mathcal{E}(\vec{k}))\right] = \frac{\langle n_{\vec{k}}\rangle_-}{1 - \langle n_{\vec{k}}\rangle_-}.$$

This enables us to write the joint probability as

$$P(\{n_{\vec{k}}\}) = \prod_{\vec{k}} \left[\left(\langle n_{\vec{k}}\rangle_-\right)^{n_{\vec{k}}} \left(1 - \langle n_{\vec{k}}\rangle_-\right)^{1-n_{\vec{k}}}\right].$$

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(c) A random variable has a set of ℓ discrete outcomes with probabilities p_n, where $n = 1, 2, \cdots, \ell$. What is the entropy of this probability distribution? What is the maximum possible entropy?

• A random variable has a set of ℓ discrete outcomes with probabilities p_n. The entropy of this probability distribution is calculated from

$$S = -k_B \sum_{n=1}^{\ell} p_n \ln p_n \quad .$$

The maximum entropy is obtained if all probabilities are equal, $p_n = 1/\ell$, and given by $S_{max} = k_B \ln \ell$.

(d) Calculate the entropy of the probability distribution for fermion occupation numbers in part (b), and comment on its zero temperature limit.

• Since the occupation numbers of different one-particle states are independent, the corresponding entropies are additive, and given by

$$S = -k_B \sum_{\vec{k}} \left[\langle n_{\vec{k}} \rangle_- \ln \langle n_{\vec{k}} \rangle_- + \left(1 - \langle n_{\vec{k}} \rangle_- \right) \ln \left(1 - \langle n_{\vec{k}} \rangle_- \right) \right] .$$

In the zero temperature limit all occupation numbers are either 0 or 1. In either case the contribution to entropy is zero, and the fermi system at $T = 0$ has zero entropy.

(e) Calculate the variance of the total number of particles $\langle N^2 \rangle_c$, and comment on its zero temperature behavior.

• The total number of particles is given by $N = \sum_{\vec{k}} n_{\vec{k}}$. Since the occupation numbers are independent

$$\langle N^2 \rangle_c = \sum_{\vec{k}} \langle n_{\vec{k}}^2 \rangle_c = \sum_{\vec{k}} \left(\langle n_{\vec{k}}^2 \rangle_- - \langle n_{\vec{k}} \rangle_-^2 \right) = \sum_{\vec{k}} \langle n_{\vec{k}} \rangle_- \left(1 - \langle n_{\vec{k}} \rangle_- \right),$$

since $\langle n_{\vec{k}}^2 \rangle_- = \langle n_{\vec{k}} \rangle_-$. Again, since at $T = 0$, $\langle n_{\vec{k}} \rangle_- = 0$ or 1, the variance $\langle N^2 \rangle_c$ vanishes.

(f) The number fluctuations of a gas is related to its compressibility κ_T, and number density $n = N/V$, by

$$\langle N^2 \rangle_c = N n k_B T \kappa_T \quad .$$

Give a *numerical estimate* of the compressibility of the fermi gas in a metal at $T = 0$ in units of $\mathring{A}^3 eV^{-1}$.

• To obtain the compressibility from $\langle N^2 \rangle_c = N n k_B T \kappa_T$, we need to examine the behavior at small but finite temperatures. At small but finite T, a small fraction of states around the fermi energy have occupation numbers around $1/2$. The number of such states is roughly $N k_B T / \varepsilon_F$, and hence we can estimate the variance as

$$\langle N^2 \rangle_c = N n k_B T \kappa_T \approx \frac{1}{4} \times \frac{N k_B T}{\varepsilon_F}.$$

The compressibility is then approximates as

$$\kappa_T \approx \frac{1}{4 n \varepsilon_F},$$

where $n = N/V$ is the density. For electrons in a typical metal $n \approx 10^{29} m^{-3} \approx 0.1 \mathring{A}^3$, and $\varepsilon_F \approx 5 eV \approx 5 \times 10^{4}\,{}^\circ K$, resulting in

$$\kappa_T \approx 0.5 \mathring{A}^3 eV^{-1}.$$

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