G25.2651: Advanced Statistical Mechanics

Midterm Exam

Instructions: This is a closed-book exam. No notes or textbooks are permitted. Partial credit will be given, so be sure to show *all* your work and to present it in a neat an organized fashion.

Maximum point value: 100

1. (**20 points**)
An ideal gas of N massless classical particles in a container of volume V at temperature T is described by a Hamiltonian of the form

$$\mathcal{H} = \sum_{i=1}^{N} c|\mathbf{p}_i|$$

where c is a constant.

   a. (**10 points**)
   Calculate the canonical partition function $Q(N, V, T)$.

   Hint: Try transforming the momentum integrations to spherical-polar variables.

   b. (**5 points**)
   Determine the equation of state.

   c. (**5 points**)
   Calculate the average internal energy

$$E = -\left(\frac{\partial \ln Q}{\partial \beta}\right)$$

2. (**25 points**)
A single particle in one spatial dimension with coordinate q and momentum p moves in a quartic potential given by

$$U(q) = \frac{1}{2}\kappa q^2 + g q^4$$

where κ and g are constants. In this problem, we will show that even for an anharmonic potential such as this, the canonical partition function can be evaluated as an infinite power series.

   a. (**5 points**)
   Write down the full canonical partition function $Q(\beta)$, where $\beta = 1/kT$, for this system, including the correct prefactor.

   b. (**5 points**)
   Using the expansion

$$e^{-\beta g q^4} = \sum_{n=0}^{\infty} (-1)^n \frac{(\beta g)^n}{n!} q^{4n}$$

   express the partition function as an infinite sum of phase space integrals.

c. (**5 points**)
Show that integrals of the general form

$$\int_{-\infty}^{\infty} dq\; q^{4n} e^{-\alpha q^2}$$

can be evaluated as

$$\int_{-\infty}^{\infty} dq\; q^{4n} e^{-\alpha q^2} = \frac{\partial^{2n}}{\partial \alpha^{2n}} \int_{-\infty}^{\infty} dq\; e^{-\alpha q^2} = \frac{\partial^{2n}}{\partial \alpha^{2n}} \sqrt{\frac{\pi}{\alpha}} = \frac{(4n-1)!!}{(2\alpha)^{2n}} \sqrt{\frac{\pi}{\alpha}}$$

where $N!! \equiv 1 \cdot 3 \cdot 5 \cdot 7 \cdots N$.

d. (**10 points**)
Using the above formula, evaluate each of the phase space integrals appearing in part b and obtain a final expression for the partition function as an infinite series.

3. (**20 points**)
Consider a classical system described by a phase space vector x and Hamiltonian $\mathcal{H}(\mathrm{x})$. Assume the system contains N identical particles. Let us introduce a new ensemble for describing a system with volume V and internal energy E called the *Gaussian* ensemble whose partition function is

$$\Gamma(N, V, E, \sigma) = \frac{E_0}{N! h^{3N}} \left(\frac{1}{2\pi\sigma^2} \right)^{1/2} \int d\mathrm{x}\; e^{-(\mathcal{H}(\mathrm{x}) - E)^2/2\sigma^2}$$

where E_0 and σ are additional parameters. Note that the microcanonical partition function $\Omega(N, V, E)$ is given as a limit of the Gaussian partition function:

$$\Omega(N, V, E) = \lim_{\sigma \to 0} \Gamma(N, V, E, \sigma)$$

a. (**5 points**)
Using the thermodynamic relation

$$\frac{1}{kT} = \left(\frac{\partial \ln \Gamma(N, V, E, \sigma)}{\partial E} \right)_{N,V}$$

prove that the average energy in the Gaussian ensemble is given by

$$\langle \mathcal{H}(\mathrm{x}) \rangle = E + \frac{\sigma^2}{kT}$$

b. (**5 points**)
Show that in the limit $\sigma \to 0$, the above relation reduces to the constant energy condition $\mathcal{H}(\mathrm{x}) = E$ of the microcanonical ensemble.

c. (**10 points**)
If the phase space is represented in terms of Cartesian coordinates $\mathbf{r}_1, ..., \mathbf{r}_N$ and conjugate momenta $\mathbf{p}_1, ..., \mathbf{p}_N$ and the system occupies a container of volume V, then by introducing scaled phase space variables

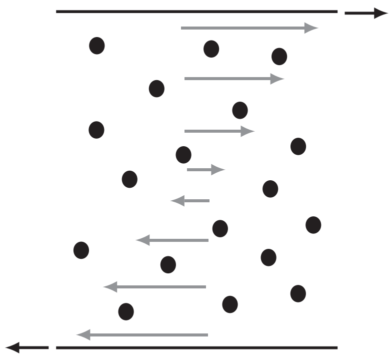
$$\mathbf{s}_i = V^{-1/3} \mathbf{r}_i, \qquad \boldsymbol{\pi}_i = V^{1/3} \mathbf{p}_i$$

into the partition function for the Gaussian ensemble, use pressure definition

$$\frac{P}{kT} = \left(\frac{\partial \ln \Gamma(N, V, E, \sigma)}{\partial V} \right)_{N,E}$$

to derive a phase space function $p(\mathbf{p}, \mathbf{r})$ that serves as an estimator for the pressure.

4. (**35 points**)
Consider a classical N-particle system that is subject to an external shearing force. Such a force can be imposed by placing the system between parallel plates and pulling the plates in opposite directions as illustrated in the figure below.



If the system is a liquid, then it will flow in layers with the maximal flow rate occuring closest to the plates. This flow pattern is known as a *flow profile*, and we can take this profile to be an approximately linear function. That is, if the plates are perpendicular to the y-axis, then the flow rate of the liquid at position y will be given by the linear form γy, where γ is known as the shear rate.

Let $\hat{\mathbf{x}} = (1,0,0)$, $\hat{\mathbf{y}} = (0,1,0)$, and $\hat{\mathbf{z}} = (0,0,1)$ be the unit vectors along the x, y, and z directions, and let $\mathbf{r}_1, ..., \mathbf{r}_N$ be the Cartesian positions of the particles and $\mathbf{p}_1, ..., \mathbf{p}_N$ be their conjugate momenta. Suppose, further, that the particles interact via a potential $U(\mathbf{r}_1, ..., \mathbf{r}_N)$, then a set of microscopic equations of motion capable of describing the motion of the system subject to an external shear is

$$\begin{aligned} \dot{\mathbf{r}}_i &= \frac{\mathbf{p}_i}{m_i} + (\mathbf{r}_i \cdot \hat{\mathbf{y}})\,\gamma\hat{\mathbf{x}} \\ \dot{\mathbf{p}}_i &= \mathbf{F}_i - (\mathbf{p}_i \cdot \hat{\mathbf{y}})\,\gamma\hat{\mathbf{x}} \end{aligned} \tag{1}$$

a. (**5 points**)
Show that the phase space compressibility

$$\kappa = \sum_{i=1}^{N} \left[\nabla_{\mathbf{r}_i} \cdot \dot{\mathbf{r}}_i + \nabla_{\mathbf{p}_i} \cdot \dot{\mathbf{p}}_i\right]$$

vanishes for this set of equations of motion.

b. (**5 points**)
Prove that the following energy function

$$\mathcal{H}' = \sum_{i=1}^{N} \frac{1}{2m_i} \left[\mathbf{p}_i + m_i\,(\mathbf{r}_i \cdot \hat{\mathbf{y}})\,\gamma\hat{\mathbf{x}}\right]^2 + U(\mathbf{r}_1, ..., \mathbf{r}_N)$$

is *not* a Hamiltonian for this system.

Hint: Try proof by contradiction. That is, prove that the equations of motion derived from $\mathcal{H}'$ are *not* the microscopic equations given by Eqns. (1).

c. (**5 points**)
Prove, nevertheless, that $\mathcal{H}'$ is conserved by Eqns. (1).

d. (**5 points**)
Show that the physical Hamiltonian of the system

$$\mathcal{H} = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m_i} + U(\mathbf{r}_1, ..., \mathbf{r}_N)$$

is *not* conserved by Eqns. (1). What is $d\mathcal{H}/dt$ if it is not zero?

e. (**2 points**)
Can this system ever reach equilibrium for nonzero γ? Explain your answer.

f. (**5 points**)
Now consider dividing the system up into thin slabs perpendicular to the y-axis. Assume that each slab is sufficiently thin to contain roughly a single monolayer of the liquid. If particle i is in a slab located at position y along the y-axis, then we can assume that $y_i \approx y$, where y_i is the y-component of the particle's position vector $\mathbf{r}_i$.

Within a given slab, the flow rate, γy is approximately constant. Therefore, consider transforming, within the slab, to a frame that moves with the fluid at a constant velocity γy. Determine the velocity $\mathbf{v}_i'$ and momentum $\mathbf{p}_i'$ of particle i in this moving frame.

g. (**5 points**)
Assuming that diffusion of particles between slabs can be neglected, show that the motion of particles in a given slab is approximately Hamiltonian in the frame of part f, and derive the corresponding equations of motion and conserved Hamiltonian.

h. (**3 points**)
In light of the result of part g, is it possible to regard each slab as an equilibrium ensemble? If so, determine the partition function of this ensemble. If not, explain why this is not possible. In either case, is your answer consistent with that of part e? Explain.