CHEM-GA 2651: Statistical Mechanics

Midterm Exam

Instructions: This is a closed-book exam, however, notes taken in class during lectures (and only these) 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. Write all of your solutions in the blue books provided.

Maximum point value: 100

1. (**20 points**)

   a. (**15 points**)
   Prove that the relative volume fluctuations $\Delta V/\langle V\rangle$, where

   $$\Delta V = \sqrt{\langle V^2\rangle - \langle V\rangle^2}$$

   in the isothermal-isobaric ensemble are given by

   $$\frac{\Delta V}{\langle V\rangle} = \sqrt{\frac{kT\kappa_T}{\langle V\rangle}}$$

   where κ_T is the isothermal compressibility given by

   $$\kappa_T = -\frac{1}{\langle V\rangle}\left(\frac{\partial\langle V\rangle}{\partial P}\right)_{N,T}.$$

   b. (**5 points**)
   Show that $\Delta V/\langle V\rangle$ in the thermodynamic limit.

2. (**40 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. (**20 points**)
   Calculate the canonical partition function $Q(N,V,T)$.

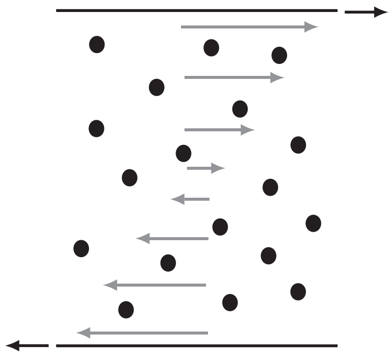
   Hint: Try transforming the momentum integrations to spherical-polar variables.

   b. (**10 points**)
   Determine the equation of state.

   c. (**10 points**)
   Calculate the average internal energy

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

3. (**40 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

$$\dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m_i} + (\mathbf{r}_i \cdot \hat{\mathbf{y}})\, \gamma \hat{\mathbf{x}}$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i - (\mathbf{p}_i \cdot \hat{\mathbf{y}})\, \gamma \hat{\mathbf{x}} \tag{1}$$

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. (**10 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.