

# ANSWERS TO PROBLEM SET 1

## 1 Properties of the Liouville Operator

- a. Give the equations of motion in terms of the Hamiltonian. Show that they can be rewritten in the form

$$\begin{aligned}\frac{d\mathbf{x}^{(N)}}{dt} &= \{\mathbf{x}^{(N)}, H\} \\ &= \mathcal{L} \mathbf{x}^{(N)}.\end{aligned}$$

Answer:

The equations of motion in terms of the Hamiltonian are

$$\begin{aligned}\frac{d\mathbf{r}^{(N)}}{dt} &= \frac{\partial H}{\partial \mathbf{p}^{(N)}} \\ \frac{d\mathbf{p}^{(N)}}{dt} &= -\frac{\partial H}{\partial \mathbf{r}^{(N)}}\end{aligned}$$

To rewrite these in the desired form, note that

$$\frac{\partial \mathbf{r}^{(N)}}{\partial \mathbf{r}^{(N)}} = \mathbb{1}, \quad \frac{\partial \mathbf{r}^{(N)}}{\partial \mathbf{p}^{(N)}} = 0, \quad \frac{\partial \mathbf{p}^{(N)}}{\partial \mathbf{r}^{(N)}} = 0, \quad \frac{\partial \mathbf{p}^{(N)}}{\partial \mathbf{p}^{(N)}} = \mathbb{1},$$

so that one can write

$$\begin{aligned}\frac{d\mathbf{r}^{(N)}}{dt} &= \frac{\partial \mathbf{r}^{(N)}}{\partial \mathbf{r}^{(N)}} \cdot \frac{\partial H}{\partial \mathbf{p}^{(N)}} = \frac{\partial \mathbf{r}^{(N)}}{\partial \mathbf{r}^{(N)}} \cdot \frac{\partial H}{\partial \mathbf{p}^{(N)}} - \frac{\partial \mathbf{r}^{(N)}}{\partial \mathbf{p}^{(N)}} \cdot \frac{\partial H}{\partial \mathbf{r}^{(N)}} = \{\mathbf{r}^{(N)}, H\} = \mathcal{L} \mathbf{r}^{(N)} \\ \frac{d\mathbf{p}^{(N)}}{dt} &= -\frac{\partial \mathbf{p}^{(N)}}{\partial \mathbf{p}^{(N)}} \cdot \frac{\partial H}{\partial \mathbf{r}^{(N)}} = \frac{\partial \mathbf{p}^{(N)}}{\partial \mathbf{r}^{(N)}} \cdot \frac{\partial H}{\partial \mathbf{p}^{(N)}} - \frac{\partial \mathbf{p}^{(N)}}{\partial \mathbf{p}^{(N)}} \cdot \frac{\partial H}{\partial \mathbf{r}^{(N)}} = \{\mathbf{p}^{(N)}, H\} = \mathcal{L} \mathbf{p}^{(N)}.\end{aligned}$$

With  $\mathbf{x}^{(N)} = (\mathbf{r}^{(N)}, \mathbf{p}^{(N)})$ , this is the desired form.

- b. Show that  $\mathbf{P} = \sum_{i=1}^N \mathbf{p}_i$  is a constant of the motion.

Answer:

$\mathbf{P}$  is a constant of the motion if  $d\mathbf{P}/dt = 0$ . Since  $d\mathbf{P}/dt = \mathcal{L}\mathbf{P} = \{\mathbf{P}, H\}$ , we need to show that  $\{\mathbf{P}, H\} = 0$ . Now:

$$\{\mathbf{P}, H\} = -\frac{\partial \mathbf{P}}{\partial \mathbf{p}^{(N)}} \cdot \frac{\partial H}{\partial \mathbf{r}^{(N)}} = -\sum_{i=1}^N \frac{\partial U}{\partial \mathbf{r}_i}$$

$$\begin{aligned}
&= -\frac{1}{2} \sum_{i=1}^N \frac{\partial}{\partial \mathbf{r}_i} \sum_{j \neq k} U(|\mathbf{r}_j - \mathbf{r}_k|) \\
&= -\frac{1}{2} \sum_{i=1}^N \sum_{j \neq k} U'(|\mathbf{r}_j - \mathbf{r}_k|) \frac{\partial |\mathbf{r}_j - \mathbf{r}_k|}{\partial \mathbf{r}_i} \\
&= -\frac{1}{2} \sum_{i=1}^N \sum_{j \neq k} U'(|\mathbf{r}_j - \mathbf{r}_k|) \frac{\mathbf{r}_j - \mathbf{r}_k}{|\mathbf{r}_j - \mathbf{r}_k|} (\delta_{ij} - \delta_{ik}) \\
&= -\frac{1}{2} \sum_{j \neq k} U'(|\mathbf{r}_j - \mathbf{r}_k|) \frac{\mathbf{r}_j - \mathbf{r}_k}{|\mathbf{r}_j - \mathbf{r}_k|} (1 - 1) = 0.
\end{aligned}$$

which proves that  $\mathbf{P}$  is a constant of the motion.

- c. Given functions of phase space  $A(\mathbf{x}^{(N)})$ ,  $B(\mathbf{x}^{(N)})$ ,  $C(\mathbf{x}^{(N)})$ , prove the following properties of the Poisson brackets:

$$\begin{aligned}
\{AB, C\} &= A\{B, C\} + B\{A, C\} \\
\{A, F(B)\} &= \frac{dF}{dB}\{A, B\},
\end{aligned}$$

where  $F(B)$  is a function of  $B$  that only depends on the phase coordinate  $\mathbf{x}^{(N)}$  through  $B$ .

Answer:

For the first identity the left hand side gives

$$\begin{aligned}
\{AB, C\} &= \frac{\partial(AB)}{\partial \mathbf{r}^{(N)}} \cdot \frac{\partial C}{\partial \mathbf{p}^{(N)}} - \frac{\partial(AB)}{\partial \mathbf{p}^{(N)}} \cdot \frac{\partial C}{\partial \mathbf{r}^{(N)}} \\
&= A \frac{\partial B}{\partial \mathbf{r}^{(N)}} \cdot \frac{\partial C}{\partial \mathbf{p}^{(N)}} + B \frac{\partial A}{\partial \mathbf{r}^{(N)}} \cdot \frac{\partial C}{\partial \mathbf{p}^{(N)}} - A \frac{\partial B}{\partial \mathbf{p}^{(N)}} \cdot \frac{\partial C}{\partial \mathbf{r}^{(N)}} - B \frac{\partial A}{\partial \mathbf{p}^{(N)}} \cdot \frac{\partial C}{\partial \mathbf{r}^{(N)}} \\
&= A \left( \frac{\partial B}{\partial \mathbf{r}^{(N)}} \cdot \frac{\partial C}{\partial \mathbf{p}^{(N)}} - \frac{\partial B}{\partial \mathbf{p}^{(N)}} \cdot \frac{\partial C}{\partial \mathbf{r}^{(N)}} \right) + B \left( \frac{\partial A}{\partial \mathbf{r}^{(N)}} \cdot \frac{\partial C}{\partial \mathbf{p}^{(N)}} - \frac{\partial A}{\partial \mathbf{p}^{(N)}} \cdot \frac{\partial C}{\partial \mathbf{r}^{(N)}} \right) \\
&= A\{B, C\} + B\{A, C\}.
\end{aligned}$$

So the first identity is proved.

Similarly, for the second identity we also write out the left hand side:

$$\begin{aligned}
\{A, F(B)\} &= \frac{\partial A}{\partial \mathbf{r}^{(N)}} \cdot \frac{\partial F(B)}{\partial \mathbf{p}^{(N)}} - \frac{\partial A}{\partial \mathbf{p}^{(N)}} \cdot \frac{\partial F(B)}{\partial \mathbf{r}^{(N)}} \\
&= \frac{\partial A}{\partial \mathbf{r}^{(N)}} \cdot \frac{\partial B}{\partial \mathbf{p}^{(N)}} \frac{\partial F}{\partial B} - \frac{\partial A}{\partial \mathbf{p}^{(N)}} \cdot \frac{\partial B}{\partial \mathbf{r}^{(N)}} \frac{\partial F}{\partial B} \\
&= \{A, B\} \frac{dF}{dB}.
\end{aligned}$$

So the second identity is proved as well.

d. Prove that

$$\mathcal{L}(AB) = A\mathcal{L}B + B\mathcal{L}A.$$

Answer:

Once more we evaluate the left hand side, using the first identity:

$$\begin{aligned}\mathcal{L}(AB) &= \{AB, H\} = A\{B, H\} + B\{A, H\} \\ &= A\mathcal{L}B + B\mathcal{L}A,\end{aligned}$$

which is what we set out to show.

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e. Show that

$$e^{t\mathcal{L}}(AB) = (e^{t\mathcal{L}}A)(e^{t\mathcal{L}}B).$$

Answer:

Expand out the exponent:

$$e^{t\mathcal{L}}(AB) = \sum_{n=0}^{\infty} \frac{t^n \mathcal{L}^n}{n!}(AB)$$

The result of d. shows that  $\mathcal{L}$  acts as a differential operator. The binomial theorem then tells us that

$$\begin{aligned}\mathcal{L}^n(AB) &= \sum_{i=0}^n \binom{n}{i} (\mathcal{L}^{n-i}A)(\mathcal{L}^iB) \\ &= \sum_{i=0}^n \frac{n!}{(n-i)!i!} (\mathcal{L}^{n-i}A)(\mathcal{L}^iB).\end{aligned}$$

So

$$\begin{aligned}e^{t\mathcal{L}}(AB) &= \sum_{n=0}^{\infty} \sum_{i=0}^n \frac{t^n}{(n-i)!i!} (\mathcal{L}^{n-i}A)(\mathcal{L}^iB). \\ &= \sum_{n=0}^{\infty} \sum_{i=0}^n \frac{[t\mathcal{L}]^{n-i}A}{(n-i)!} \frac{([t\mathcal{L}]^iB)}{i!}. \\ &= \sum_{i=0}^{\infty} \sum_{n=i}^{\infty} \frac{[t\mathcal{L}]^{n-i}A}{(n-i)!} \frac{([t\mathcal{L}]^iB)}{i!},\end{aligned}$$

where we exchanged the two summations, noticing that we are summing over  $n$  and  $i$  values over all non-negative values such that  $i \leq n$ . We shift the lower bound of the  $n$  summation to zero by introducing  $k = n - i$ , and get

$$\begin{aligned}&= \sum_{i=0}^{\infty} \sum_{k=0}^{\infty} \frac{[t\mathcal{L}]^kA}{k!} \frac{([t\mathcal{L}]^iB)}{i!} \\ &= \sum_{k=0}^{\infty} \frac{[t\mathcal{L}]^kA}{k!} \sum_{i=0}^{\infty} \frac{([t\mathcal{L}]^iB)}{i!} \\ &= (e^{t\mathcal{L}}A)(e^{t\mathcal{L}}B)\end{aligned}$$

which is what we were after.

This result may be understood by interpreting the operator  $e^{\mathcal{L}t}$  a streaming operator that when acting on any quantity depending in  $\mathbf{x}^{(N)}$ , replaces  $\mathbf{x}^{(N)}$  by  $\mathbf{x}^{(N)}(t)$ . Therefore  $(AB)|_{\mathbf{x}^{(N)} \rightarrow \mathbf{x}^{(N)}(t)} = A|_{\mathbf{x}^{(N)} \rightarrow \mathbf{x}^{(N)}(t)} B|_{\mathbf{x}^{(N)} \rightarrow \mathbf{x}^{(N)}(t)}$  follows automatically.

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f. Show that

$$\langle A(t + \tau)B(\tau) \rangle = \langle A(t)B(0) \rangle$$

where  $\langle \dots \rangle$  is the canonical ensemble average.

Answer:

Write

$$\begin{aligned} \langle A(t + \tau)B(\tau) \rangle &= \frac{\int d\mathbf{x}^{(N)} e^{-\beta H} \left( e^{\mathcal{L}\tau} B \right) \left( e^{\mathcal{L}(t+\tau)} A \right)}{\int d\mathbf{x}^{(N)} e^{-\beta H}} \\ &= \frac{\int d\mathbf{x}^{(N)} e^{-\beta H} e^{\mathcal{L}\tau} \left( B e^{\mathcal{L}t} A \right)}{\int d\mathbf{x}^{(N)} e^{-\beta H}} \\ &= \frac{\int d\mathbf{x}^{(N)} e^{\mathcal{L}\tau} \left( \left[ e^{-\mathcal{L}\tau} e^{-\beta H} \right] B e^{\mathcal{L}t} A \right)}{\int d\mathbf{x}^{(N)} e^{-\beta H}} \\ &= \frac{\int d\mathbf{x}^{(N)} e^{\mathcal{L}\tau} \left( e^{-\beta H} B e^{\mathcal{L}t} A \right)}{\int d\mathbf{x}^{(N)} e^{-\beta H}} \end{aligned}$$

where in the last step we have used that  $\mathcal{L}e^{-\beta H} = -\beta e^{-\beta H} \mathcal{L}H = 0$ , so  $e^{-\mathcal{L}\tau} e^{-\beta H} = e^{-\beta H}$ . As our final step, we note that  $e^{\mathcal{L}\tau}$  replaces all  $\mathbf{x}^{(N)}$  by  $\mathbf{x}^{(N)}(\tau)$ . Since the system is deterministic, this is a one-to-one mapping in phase space. It is thus possible to change our integration variables from  $\mathbf{x}^{(N)}$  to  $\mathbf{x}^{(N)}(\tau)$ . The Jacobian of this transformation is one due to Liouville's theorem, so

$$\begin{aligned} &= \frac{\int d\mathbf{x}^{(N)}(t) \left( e^{-\beta H} B e^{\mathcal{L}t} A \right) \Big|_{\mathbf{x}^{(N)} \rightarrow \mathbf{x}^{(N)}(\tau)}}{\int d\mathbf{x}^{(N)} e^{-\beta H}} \\ &= \frac{\int d\mathbf{x}^{(N)} e^{-\beta H} B e^{\mathcal{L}t} A}{\int d\mathbf{x}^{(N)} e^{-\beta H}} \end{aligned}$$

where we renamed  $\mathbf{x}^{(N)}(t)$  to  $\mathbf{x}^{(N)}$ . The right hand side is now equal to  $\langle A(t)B(0) \rangle$ , as we wanted to show.

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g. Show that the Fourier transform of the density  $A(\mathbf{r}) = \sum_{i=1}^N a_i \delta(\mathbf{r} - \mathbf{r}_i)$ , where  $a_i$  is some microscopic function of  $\mathbf{x}_i$ , is equal to

$$A_{\mathbf{k}} = \sum_{i=1}^N a_i e^{i\mathbf{k} \cdot \mathbf{r}_i}.$$

What are the restrictions on the wave vectors  $\mathbf{k}$  for the periodic system?

Answer:

We take the Fourier transform of the that density:

$$\int_V d\mathbf{r} e^{i\mathbf{k}\cdot\mathbf{r}} A(\mathbf{r}) = \int_V d\mathbf{r} e^{i\mathbf{k}\cdot\mathbf{r}} \sum_{i=1}^N a_i \delta(\mathbf{r} - \mathbf{r}_i) = \sum_{i=1}^N \int_V d\mathbf{r} e^{i\mathbf{k}\cdot\mathbf{r}} a_i \delta(\mathbf{r} - \mathbf{r}_i) = \sum_{i=1}^N e^{i\mathbf{k}\cdot\mathbf{r}_i} a_i,$$

as we were requested to show.

The wave vectors are restricted because the corresponding wavelengths  $\lambda = 2\pi/k$  have to 'fit' into the box, i.e.  $n\lambda = L$ , where  $n$  is an integer number. This has to occur in each direction, so if  $\mathbf{k} = (k_x, k_y, k_z)$ , we need  $n_x 2\pi/k_x = L$ ,  $n_y 2\pi/k_y = L$  and  $n_z 2\pi/k_z = L$ , or

$$k_x = \frac{2\pi}{L} n_x, \quad k_y = \frac{2\pi}{L} n_y, \quad k_z = \frac{2\pi}{L} n_z$$

h. Prove that given two wave vectors  $\mathbf{k}$  and  $\mathbf{q}$ , one has

$$\begin{aligned} \langle A_{\mathbf{k}}(t) A_{\mathbf{q}} \rangle &= \delta_{\mathbf{k}, -\mathbf{q}} \langle A_{\mathbf{k}}(t) A_{-\mathbf{k}} \rangle \\ &= \delta_{\mathbf{k}, -\mathbf{q}} \langle A_{\mathbf{k}}(t) A_{\mathbf{k}}^* \rangle, \end{aligned}$$

Answer:

Writing out the left hand side gives:

$$\begin{aligned} \langle A_{\mathbf{k}}(t) A_{\mathbf{q}} \rangle &= \frac{\int d\mathbf{x}^{(N)} e^{-\beta H} \sum_{i=1}^N \sum_{j=1}^N e^{i\mathbf{k}\cdot\mathbf{r}_i(t) + i\mathbf{q}\cdot\mathbf{r}_j(0)}}{\int d\mathbf{x}^{(N)} e^{-\beta H}} \\ &= \frac{\int d\mathbf{r}^{(N)} e^{-\beta U} \sum_{i=1}^N \sum_{j=1}^N e^{i\mathbf{k}\cdot\mathbf{r}_i(t) + i\mathbf{q}\cdot\mathbf{r}_j(0)}}{\int d\mathbf{r}^{(N)} e^{-\beta U}} \end{aligned}$$

Because  $U$  depends only of position differences, it does not change under a translation over a constant vector  $\mathbf{a}$ , so we may write the same quantity as

$$\langle A_{\mathbf{k}}(t) A_{\mathbf{q}} \rangle = \frac{\int d\mathbf{r}^{(N)} e^{-\beta U} \sum_{i=1}^N \sum_{j=1}^N e^{i\mathbf{k}\cdot(\mathbf{r}_i(t) + \mathbf{a}) + i\mathbf{q}\cdot(\mathbf{r}_j(0) + \mathbf{a})}}{\int d\mathbf{r}^{(N)} e^{-\beta U}}$$

We have used here that when the system is translated over a vector  $\mathbf{a}$  at time zero, at time  $t$  it will still be translated over the same amount, i.e., the dynamics of the relative motions are not affected by our translation.

We can take the parts involving  $\mathbf{a}$  out of the integral, which yields

$$\langle A_{\mathbf{k}}(t) A_{\mathbf{q}} \rangle = e^{i(\mathbf{k} + \mathbf{q}) \cdot \mathbf{a}} \langle A_{\mathbf{k}}(t) A_{\mathbf{q}} \rangle$$

or

$$(1 - e^{i(\mathbf{k}+\mathbf{q})\cdot\mathbf{a}})\langle A_{\mathbf{k}}(t)A_{\mathbf{q}} \rangle = 0.$$

Therefore,  $\langle A_{\mathbf{k}}(t)A_{\mathbf{q}} \rangle$  is zero unless

$$e^{i(\mathbf{k}+\mathbf{q})\cdot\mathbf{a}} = 1.$$

Since this is to hold for all  $\mathbf{a}$ , this means we get a non-zero result only when  $\mathbf{k} = -\mathbf{q}$ . Another way to formulate this is

$$\langle A_{\mathbf{k}}(t)A_{\mathbf{q}} \rangle = \delta_{\mathbf{k},-\mathbf{q}}\langle A_{\mathbf{k}}(t)A_{-\mathbf{k}} \rangle$$

Finally, we can note that using complex conjugation,

$$A_{-\mathbf{k}} = \sum_{n=1}^N a_n e^{-i\mathbf{k}\cdot\mathbf{r}_n} = \left( \sum_{n=1}^N a_n e^{i\mathbf{k}\cdot\mathbf{r}_n} \right)^* = A_{\mathbf{k}}^*,$$

so also

$$\langle A_{\mathbf{k}}(t)A_{\mathbf{q}} \rangle = \delta_{\mathbf{k},-\mathbf{q}}\langle A_{\mathbf{k}}(t)A_{\mathbf{k}}^* \rangle.$$

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## 2 Isotropy

a.  $\int_V d\mathbf{r} A(\mathbf{r}) \mathbf{r} = 0,$

Answer:

Since  $A$  depends only on  $\mathbf{r}$ , we can change the integration variable to  $-\mathbf{r}$  (i.e., perform a reflection) and get

$$\int_V d\mathbf{r} A(\mathbf{r}) \mathbf{r} = - \int_V d\mathbf{r} A(\mathbf{r}) \mathbf{r},$$

that is, the result must be equal to minus itself. This can only be true if the result is zero.

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b.  $\int_V d\mathbf{r} A(\mathbf{r}) \mathbf{r} \mathbf{r} = \frac{1}{3} \int_V d\mathbf{r} A(\mathbf{r}) |\mathbf{r}|^2 \mathbb{1},$

where  $\mathbb{1}$  is the identity matrix.

Answer:

Let us call the result  $\mathbf{M}$ , i.e.,

$$\mathbf{M} = \int_V d\mathbf{r} A(\mathbf{r}) \mathbf{r} \mathbf{r}$$

This is a matrix. If we consider the  $xy$  component, and perform a reflection in the  $x$  direction only, we see that

$$M_{xy} = \int_V d\mathbf{r} A(\mathbf{r}) xy = - \int_V d\mathbf{r} A(\mathbf{r}) xy = -M_{xy}$$

so  $M_{xy} = 0$ . In the same way, we find  $M_{yz} = 0$  and  $M_{xz} = 0$ . Thus  $M$  is a diagonal matrix:

$$M = \begin{pmatrix} M_{xx} & 0 & 0 \\ 0 & M_{yy} & 0 \\ 0 & 0 & M_{zz} \end{pmatrix}.$$

In addition, because  $A$  only depends on the magnitude of  $\mathbf{r}$ , we may also use a rotation as a change of variables, i.e.  $\mathbf{r} \rightarrow R \cdot \mathbf{r}$ , which gives

$$\begin{aligned} M &= \int_V d\mathbf{r} A(\mathbf{r}) \mathbf{r} \mathbf{r} \\ &= \int_V d\mathbf{r} A(\mathbf{r}) (\mathcal{R} \cdot \mathbf{r})(\mathcal{R} \cdot \mathbf{r}) \\ &= \mathcal{R} \cdot M \cdot \mathcal{R}^T. \end{aligned}$$

In other words,  $M$  is invariant under all rotations. Take as a special case the rotation

$$\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{1}$$

This transforms  $M$  as follows:

$$\begin{pmatrix} M_{xx} & 0 & 0 \\ 0 & M_{yy} & 0 \\ 0 & 0 & M_{zz} \end{pmatrix} \rightarrow \begin{pmatrix} M_{yy} & 0 & 0 \\ 0 & M_{xx} & 0 \\ 0 & 0 & M_{zz} \end{pmatrix} \tag{2}$$

Since both matrices need to be the same we get  $M_{xx} = M_{yy}$ . One may similarly show that  $M_{xx} = M_{zz}$ , so that the whole matrix becomes proportional to the identity matrix:

$$\begin{aligned} M &= M_{xx} \mathbb{1} \\ &= \frac{1}{3} [M_{xx} + M_{yy} + M_{zz}] \mathbb{1} \end{aligned}$$

Inserting the definition of the matrix, we get

$$M = \frac{1}{3} \int_V d\mathbf{r} A(\mathbf{r}) |\mathbf{r}|^2 \mathbb{1}.$$

### 3 Ergodicity

- a. Derive the equations of motion.

Answer:

Using  $dx/dt = \partial H/\partial p$  and  $dp/dt = \partial H/\partial r$ , we find

$$\begin{aligned}\frac{dx}{dt} &= \frac{p}{m} \\ \frac{dp}{dt} &= -m\omega^2 r.\end{aligned}$$

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- b. Give the general solution for  $x(t)$  and  $p(t)$  and show that they are periodic. What is the period  $\tau$ ?

Answer:

Substituting the equation for  $dx/dt$  into that of  $dp/dt$ , we find a second order linear ordinary differential equation for  $x(t)$ :

$$\ddot{x} = -\omega^2 x.$$

The general solution can be expressed in terms of two fundamental solutions

$$x_1(t) = \sin(\omega t) \text{ and } x_2(t) = \cos(\omega t)$$

Any linear combination  $x(t) = a x_1(t) + b x_2(t)$  is then a solution. An alternative way to write this is

$$x(t) = a \cos(\omega t - \phi_0).$$

Such a solution is fixed by two initial conditions, namely, its value at time zero ( $a \cos \phi_0$ ) and its derivative at time zero ( $a\omega \sin \phi_0$ ).

The period of these solutions is

$$\tau = \frac{2\pi}{\omega}.$$

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- c. How does the fact that  $f(x, p)$  is a probability distribution determine the value of  $\Omega$ ? Show that its value is given by  $\Omega = \tau \delta E$ .

*Hint: change variables to  $\xi = x\sqrt{m\omega^2/2}$  and  $\eta = p/\sqrt{2m}$ .*

Answer:

The fact that  $f(x, p)$  needs to be normalized determines  $\Omega$ , i.e.,

$$\int dx dp f(x, p) = \frac{1}{\Omega} \int_{E < H < E + \delta E} dx dp = 1.$$

So

$$\Omega = \int_{E < H < E + \delta E} dx dp.$$

It is convenient to write this as a difference:

$$\Omega = \int_{H < E + \delta E} dx dp - \int_{H < E} dx dp.$$

As the hint suggests, we introduce now

$$\xi = x\sqrt{m\omega^2/2} \text{ and } \eta = p/\sqrt{2m}$$

The Jacobian in going from  $(x, p)$  to  $(\xi, \eta)$  is

$$J = \left| \frac{\partial(\xi, \eta)}{\partial(x, p)} \right| = \frac{\omega}{2}$$

while in these coordinates, the Hamiltonian takes the form

$$H = \xi^2 + \eta^2.$$

Therefore, we can write

$$\Omega = \frac{2}{\omega} \left[ \int_{\xi^2 + \eta^2 < E + \delta E} d\xi d\eta - \int_{\xi^2 + \eta^2 < E} d\xi d\eta \right].$$

The first integral is the area of a circle with radius  $\sqrt{E + \delta E}$  while the second is the area of a circle with radius  $\sqrt{E}$ . Using that the area is  $\pi$  times the radius squared, we find:

$$\Omega = \frac{2\pi}{\omega} [E + \delta E - E] = \tau \delta E.$$

- d. Using the solution of the equations of motion, show that in the limit  $\delta E \rightarrow 0$ , this system is ergodic, i.e. that

$$\langle G \rangle = \overline{G}$$

where

$$\langle G \rangle = \int dx dp f(x, p) G(x, p)$$

and

$$\overline{G} = \frac{1}{\tau} \int_0^\tau d\sigma G(x(t + \sigma), p(t + \sigma)).$$

*Hint: use  $\xi$  and  $\eta$  in the integral for  $\langle G \rangle$  and go over to polar coordinates.*

Answer:

Using the hint, we write the ensemble average of  $G$  as

$$\begin{aligned}
 \langle G \rangle &= \int dx dp f(x, p) G(x, p) \\
 &= \frac{1}{\Omega} \int_{E < H < E + \delta E} dx dp G(x, p) \\
 &= \frac{2}{\omega \tau \delta E} \int_{E < \xi^2 + \eta^2 < E + \delta E} d\xi d\eta G(\xi / \sqrt{m\omega^2/2}, \eta \sqrt{2m}) \\
 &= \frac{1}{\pi \delta E} \int_0^{2\pi} d\phi \int_{\sqrt{E}}^{\sqrt{E + \delta E}} d\rho \rho G((\cos \phi)\rho / \sqrt{m\omega^2/2}, (\sin \phi)\rho \sqrt{2m})
 \end{aligned}$$

where  $\rho = \sqrt{\xi^2 + \eta^2}$  is the radial coordinate and  $\phi$  is the angle ( $\tan \phi = \xi/\eta$ ), such that  $\xi = \rho \cos \phi$ ,  $\eta = \rho \sin \phi$ .

Assuming  $\delta E$  is small, so that  $\rho$  does not vary much, we can write this as

$$\begin{aligned}
 \langle G \rangle &= \frac{1}{\pi \delta E} \int_0^{2\pi} d\phi \int_{\sqrt{E}}^{\sqrt{E + \delta E}} d\rho \rho G((\cos \phi)\sqrt{2E/(m\omega^2)}, (\sin \phi)\sqrt{2mE}) \\
 &= \frac{1}{2\pi} \int_0^{2\pi} d\phi G((\cos \phi)\sqrt{2E/(m\omega^2)}, (\sin \phi)\sqrt{2mE})
 \end{aligned}$$

We now write  $a = \sqrt{2E/(m\omega^2)}$  and  $\phi = \phi_0 - \omega(\sigma + t)$  (the latter is a change of variables with Jacobian  $\omega$ ), to get

$$\langle G \rangle = \frac{1}{\tau} \int_0^\tau d\sigma G(a \cos(\omega(\sigma + t) - \phi_0), m\omega a \sin(\omega(\sigma + t) - \phi_0)),$$

which is precisely  $\bar{G}$ .

- e. Calculate the partition function and the Helmholtz free energy  $A$ .

Answer:

The partition function is given by

$$\begin{aligned}
 Q &= \frac{1}{h} \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dp e^{-\beta H} \\
 &= \frac{1}{h} \int_{-\infty}^{\infty} dx e^{-\beta \frac{1}{2} m \omega^2 x^2} \int_{-\infty}^{\infty} dp e^{-\beta \frac{p^2}{2m}} \\
 &= \frac{2\pi}{h} \sqrt{\frac{m}{\beta}} \sqrt{\frac{1}{\beta m \omega^2}} \\
 &= \frac{2\pi}{\beta h \omega}.
 \end{aligned}$$

The Helmholtz free energy is

$$A = -kT \ln Q = kT \ln \frac{\beta h \omega}{2\pi}.$$


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- f. Calculate  $\langle H \rangle$  in the canonical ensemble. For what choice of  $\beta$  is its value equal to that of the micro-canonical ensemble?

Answer:

From the notes, we find

$$\langle H \rangle = -\frac{\partial}{\partial \beta} \ln Q = \frac{\partial}{\partial \beta} \ln[\beta h \omega / (2\pi)] = \frac{1}{\beta}.$$

Thus, if we choose  $\beta = 1/E$ , the canonical and microcanonical results for the average energy agree.

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- g. Taking the above choice for  $\beta$ , show that the value of  $\langle p^2 \rangle$  is the same in the canonical and in the micro-canonical ensemble.

Answer:

Canonical:

$$\langle p^2 \rangle_c = \int_{-\infty}^{\infty} p^2 \frac{e^{-\beta \frac{p^2}{2m}}}{\sqrt{2\pi m/\beta}} = m/\beta \hat{=} mE.$$

Micro-canonical:

$$\begin{aligned} \langle p^2 \rangle_{mc} &= \frac{1}{\Omega} \int_{E < H < E + \delta E} dx dp p^2 \\ &= \frac{4m}{\omega \Omega} \int_{E < \xi^2 + \eta^2 < E + \delta E} d\xi d\eta \eta^2 \\ &= \frac{4m}{\omega \Omega} \int_{\sqrt{E}}^{\sqrt{E + \delta E}} d\rho \int_0^{2\pi} d\phi \rho \rho^2 \cos^2 \phi \\ &= \frac{4\pi m}{\omega \Omega} \int_{\sqrt{E}}^{\sqrt{E + \delta E}} d\rho \rho^3 \\ &= \frac{\pi m}{\omega \Omega} [\rho^4]_{\rho=\sqrt{E}}^{\sqrt{E + \delta E}} \\ &= \frac{\pi m}{\omega \Omega} [(E + \delta E)^2 - E^2] \\ &\approx \frac{\pi m}{\omega \Omega} 2E\delta E = mE. \end{aligned}$$


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- h. Calculate the values of  $\langle p^4 \rangle$  in the canonical and the micro-canonical ensemble, respectively. Are these values equal? What is the consequence for  $\sigma_K^2$  in the two ensembles? Explain this result.

*Hint for g and h: for the micro-canonical value, use  $\xi$  and  $\eta$ , go over to polar coordinates and use that  $\int_0^{2\pi} d\phi \cos^2 \phi = \pi$  and  $\int_0^{2\pi} d\phi \cos^4 \phi = 3\pi/4$ .*

Answer:

Canonical:

$$\langle p^4 \rangle_c = \int_{-\infty}^{\infty} p^4 \frac{e^{-\beta \frac{p^2}{2m}}}{\sqrt{2\pi m/\beta}} = 3m^2/\beta^2 \hat{=} 3m^2 E^2.$$

Micro-canonical:

$$\begin{aligned} \langle p^4 \rangle_{mc} &= \frac{1}{\Omega} \int_{E < H < E + \delta E} dx dp p^4 \\ &= \frac{8m^2}{\omega\Omega} \int_{E < \xi^2 + \eta^2 < E + \delta E} d\xi d\eta \eta^4 \\ &= \frac{8m^2}{\omega\Omega} \int_{\sqrt{E}}^{\sqrt{E+\delta E}} d\rho \int_0^{2\pi} d\phi \rho \rho^4 \cos^4 \phi \\ &= \frac{6\pi m^2}{\omega\Omega} \int_{\sqrt{E}}^{\sqrt{E+\delta E}} d\rho \rho^5 \\ &= \frac{\pi m^2}{\omega\Omega} \left[ \rho^6 \right]_{\rho=\sqrt{E}}^{\sqrt{E+\delta E}} \\ &= \frac{\pi m^2}{\omega\Omega} [(E + \delta E)^3 - E^3] \\ &\approx \frac{\pi m^2}{\omega\Omega} 3E^2 \delta E = \frac{3}{2} m^2 E^2. \end{aligned}$$

NOT EQUAL!

Canonically:  $\sigma_K^2 = 2m^2 E^2$ ,

micro-canonically:  $\sigma_K^2 = \frac{1}{2} m^2 E^2$  ; only 1/4 of the canonical result.

Or:  $\sigma_K^{mc} = \sigma_K^c/2$ .

*So fluctuations are not the same in the two ensembles. The fluctuations in the micro-canonical ensemble are less because the energy is fixed, whereas in the canonical ensemble, the energy is allowed to vary.*

## 4 Sub-Ensembles

- a. Write down the micro-canonical probability distribution  $f(\mathbf{x}^{(N)})$  for given energy  $E$ . Show that the normalization constant  $\Omega$  as a function of the number of particles  $N$

and the energy per particle  $\varepsilon = E/N$  is to linear order in  $\delta E$  given by

$$\Omega(N, \varepsilon) = \frac{3}{\varepsilon(3N)!} \left( \frac{2\pi N\varepsilon}{\omega} \right)^{3N} \delta E.$$

*Hint: use the  $\xi, \eta$  variables of the previous problem and that the volume of a  $6N$ -dimensional sphere with radius  $r$  is  $\pi^{3N} r^{6N} / (3N)!$ .*

Answer:

The microcanonical distribution is given by

$$f(\mathbf{x}^{(N)}) = \begin{cases} \frac{1}{\Omega} & \text{if } E < H_N(\mathbf{x}^{(N)}) < E + \delta E \\ 0 & \text{otherwise.} \end{cases}$$

As a function of  $N$  and  $\varepsilon = E/N$ , the normalization constant is given by

$$\begin{aligned} \Omega(N, \varepsilon) &= \int_{N\varepsilon < H_N(\mathbf{x}^{(N)}) < N\varepsilon + \delta E} d\mathbf{x}^{(N)} \\ &= \int_{H_N(\mathbf{x}^{(N)}) < N\varepsilon + \delta E} d\mathbf{x}^{(N)} - \int_{H_N(\mathbf{x}^{(N)}) < N\varepsilon} d\mathbf{x}^{(N)} \end{aligned}$$

Going over to  $\xi^{(N)} = \mathbf{x}^{(N)} \sqrt{m\omega^2/2}$ ,  $\eta^{(N)} = \mathbf{p}^{(N)} / \sqrt{2m}$ , this becomes

$$= \left( \frac{2}{\omega} \right)^{3N} \left( \int_{|\xi^{(N)}|^2 + |\eta^{(N)}|^2 < N\varepsilon + \delta E} d\eta^{(N)} d\xi^{(N)} - \int_{|\xi^{(N)}|^2 + |\eta^{(N)}|^2 < N\varepsilon} d\eta^{(N)} d\xi^{(N)} \right).$$

The two integrals represent the volume of  $6N$ -dimensional spheres of radius  $\sqrt{N\varepsilon E + \delta E}$  and  $\sqrt{N\varepsilon}$ , respectively. The volume of such spheres is, as the hint tells us,  $\pi^{3N} r^{6N} / (3N)!$ , so

$$\begin{aligned} &= \frac{1}{(3N)!} \left( \frac{2\pi}{\omega} \right)^{3N} \left[ (N\varepsilon + \delta E)^{3N} - (N\varepsilon)^{3N} \right] \\ &\approx \frac{1}{(3N)!} \left( \frac{2\pi}{\omega} \right)^{3N} 3N(N\varepsilon)^{3N-1} \delta E \\ &= \frac{3}{\varepsilon(3N)!} \left( \frac{2\pi N\varepsilon}{\omega} \right)^{3N} \delta E. \end{aligned}$$

- b. Show that, to good approximation, the phase space distribution of the subsystem is given by

$$f_1(\mathbf{x}_1) = \frac{\Omega\left(N-1, \varepsilon + \frac{\varepsilon - H_1(\mathbf{x}_1)}{N-1}\right)}{\Omega(N, \varepsilon)}$$

Answer:

We take the definition of  $f_1$  and substitute the microcanonical distribution:

$$\begin{aligned} f_1(\mathbf{x}_1) &= \frac{1}{\Omega(N, \varepsilon)} \int_{N\varepsilon < H_N(\mathbf{x}^{(N)}) < N\varepsilon + \delta E} d\mathbf{x}_2 \dots d\mathbf{x}_N \\ &= \frac{1}{\Omega(N, \varepsilon)} \int_{N\varepsilon < [\sum_{n=1}^N H_1(\mathbf{x}_n)] < N\varepsilon + \delta E} d\mathbf{x}_2 \dots d\mathbf{x}_N \\ &= \frac{1}{\Omega(N, \varepsilon)} \int_{N\varepsilon - H_1(\mathbf{x}_1) < [\sum_{n=2}^N H_1(\mathbf{x}_n)] < N\varepsilon - H_1(\mathbf{x}_1) + \delta E} d\mathbf{x}_2 \dots d\mathbf{x}_N \end{aligned}$$

In the right hand side, we recognize the integral as the normalization of a system of  $N-1$  particles, with an average energy  $[N\varepsilon - H_1(\mathbf{x}_1)]/(N-1) = \varepsilon - \frac{H_1(\mathbf{x}_1) - \varepsilon}{N-1}$  (for this to work, we need  $N$  large so that  $N\varepsilon - H_1(\mathbf{x}_1) > 0$  because the first term is  $\mathcal{O}(N)$ , whereas the second is  $\mathcal{O}(1)$ ), so

$$= \frac{\Omega\left(N-1, \varepsilon - \frac{H_1(\mathbf{x}_1) - \varepsilon}{N-1}\right)}{\Omega(N, \varepsilon)}.$$

- c. Compute the limit  $N \rightarrow \infty$  (i.e. the limit of a large thermal bath) of  $f_1(\mathbf{x}_1)$ .

*Hint: use that  $\lim_{N \rightarrow \infty} \left(1 + \frac{a}{N}\right)^N = e^a$ .*

Answer:

We substitute the result for  $\Omega(N, \varepsilon)$  from a. into the result of b.:

$$\begin{aligned} f_1(\mathbf{x}_1) &= \frac{\Omega\left(N-1, \varepsilon + \frac{\varepsilon - H_1(\mathbf{x}_1)}{N-1}\right)}{\Omega(N, \varepsilon)} \\ &= \frac{\varepsilon(3N)! \left(\frac{2\pi(N-1)[\varepsilon + (\varepsilon - H_1)/(N-1)]}{\omega}\right)^{3N-3}}{[\varepsilon + (\varepsilon - H_1)/(N-1)](3N-3)! \left(\frac{2\pi N\varepsilon}{\omega}\right)^{3N}} \\ &= \left(\frac{\omega}{2\pi}\right)^3 \frac{\varepsilon(3N)! (N\varepsilon - H_1)^{3N-3}}{[\varepsilon + (\varepsilon - H_1)/(N-1)](3N-3)! (N\varepsilon)^{3N}} \\ &= \left(\frac{\omega}{2\pi}\right)^3 \frac{\varepsilon(3N)! (N\varepsilon - H_1)^{-3}}{[\varepsilon + (\varepsilon - H_1)/(N-1)](3N-3)!} \left(1 - \frac{3H_1/\varepsilon}{3N}\right)^{3N} \end{aligned}$$

$$\approx \left( \frac{3\omega}{2\pi\epsilon} \right)^3 e^{-3H_1/\epsilon}.$$


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- d. Show that in this limit, the subsystem is described by the canonical ensemble.

Answer:

Take

$$\beta = \frac{3}{\epsilon}.$$


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## 5 Equal-Areas Construction for Van der Waals Liquids

- a. Write the equation of state in terms of the molar volume  $\tilde{V}$ .

Answer:

$\rho$  is the number of particle (molecules) divided by the volume,  $N/V$ . if the number of particles represents  $n$  moles, we have  $\rho = nN_A/V$ , and the molar volume is the volume per mole, i.e.,  $\tilde{V} = V/n$ . Thus  $\rho = N_A/\tilde{V}$ . Substituting this into the VdW equation, we get

$$\begin{aligned} P &= \frac{kTN_A/\tilde{V}}{1 - bN_A/\tilde{V}} - \frac{aN_A^2}{\tilde{V}^2} \\ &= \frac{RT}{\tilde{V} - bN_A} - \frac{aN_A^2}{\tilde{V}^2} \end{aligned}$$

- b. Show how the conditions on the critical point,  $\partial P/\partial\tilde{V} = 0$  and  $\partial^2 P/\partial\tilde{V}^2 = 0$ , lead to

$$\tilde{V}_c = 3N_A b; \quad P_c = \frac{a}{27b^2}; \quad kT_c = \frac{8a}{27b}$$

Answer:

Call  $A = aN_A^2$  and  $B = bN_A$ . Then take the first and second derivative of  $P$  with respect to  $\tilde{V}$ , which gives

$$\frac{\partial P}{\partial\tilde{V}} = -\frac{RT}{(\tilde{V} - B)^2} + 2\frac{A}{\tilde{V}^3} = 0 \quad (3)$$

$$\frac{\partial^2 P}{\partial\tilde{V}^2} = 2\frac{RT}{(\tilde{V} - B)^3} - 6\frac{A}{\tilde{V}^4} = 0 \quad (4)$$

Multiplying the first equation by 2 and the second by  $(\tilde{V} - B)$ , leads to

$$\begin{aligned}\frac{4A}{\tilde{V}_c^3} - \frac{6(\tilde{V}_c - B)A}{\tilde{V}_c^4} &= 0 \\ 4\tilde{V}_c - 6(\tilde{V}_c - B) &= 0 \\ \tilde{V}_c &= 3B = 3bN_A.\end{aligned}$$

From (1) it follows that

$$\begin{aligned}\frac{RT_c}{(\tilde{V}_c - B)^2} &= \frac{2A}{\tilde{V}_c^3} \\ \frac{RT_c}{4B^2} &= \frac{2A}{27B^3} \\ RT_c &= \frac{8A}{27B} = \frac{8aN_A}{27b} \\ kT_c &= \frac{8A}{27B} = \frac{8a}{27b}.\end{aligned}$$

Inserting into the VdW equatin leads to

$$P_c = \frac{8A}{27B} \frac{1}{2B} - \frac{A}{9B^2} = \frac{A}{27B^2} = \frac{a}{27b^2}.$$

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c. Show that the Helmholtz free energy difference for one mole follows from

$$A(\tilde{V}_F, T) - A(\tilde{V}_B, T) = - \int_{\tilde{V}_B}^{\tilde{V}_F} d\tilde{V} P(\tilde{V}, T).$$

Answer:

Use the elementary relation

$$P = - \left( \frac{\partial A}{\partial V} \right)_{NT}$$

When we keep  $N$  and  $T$  fixed, changing the volume amounts to changing the molar volume, i.e.,

$$P = - \left( \frac{\partial A}{\partial \tilde{V}} \right)_{NT} \frac{\partial \tilde{V}}{\partial V} = - \left( \frac{\partial A}{\partial \tilde{V}} \right)_{NT} \frac{N_A}{N}$$

For one mole of substance,  $N = N_A$ , so

$$P(\tilde{V}, T) = - \left( \frac{\partial A}{\partial \tilde{V}} \right)_T$$

Integrating this at constant temperature gives

$$\int_{\tilde{V}_1}^{\tilde{V}_2} P(\tilde{V}, T) d\tilde{V} = A(\tilde{V}_1, T) - A(\tilde{V}_2, T)$$

Taking 1 = B and 2 = F leads to the desired property.

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- d. Show that the chemical potential difference (per mole)  $\mu$  can be deduced from

$$\mu(\tilde{V}_F, T) - \mu(\tilde{V}_B, T) = P(\tilde{V}_F)\tilde{V}_F - P(\tilde{V}_B)\tilde{V}_B - \int_{\tilde{V}_B}^{\tilde{V}_F} d\tilde{V} P(\tilde{V}, T).$$

Answer:

The chemical potential per mole is the Gibbs free energy  $G$  per mole, and  $G = A + PV$ . Therefore  $\mu = A(1\text{mole}) + P\tilde{V}$ , which leads to the desired result.

- e. Given the result of e., demonstrate how the fact that the liquid and the gas are in equilibrium with one another leads to the equal-areas construction.

Answer:

In equilibrium, the pressures and chemical potentials of the liquid and the gas need to be equal. That means that the right hand side of the equation from part d. must be zero, and the pressures in it must be equal, leading to

$$P(V_F - V_B) = \int_{\tilde{V}_B}^{\tilde{V}_F} d\tilde{V} P(\tilde{V}, T).$$

$P$  is the height of the plateau in the figure, so the left hand side represents the area under the plateau. The right hand side is the area under the VdW curve, and the equality states that these two are equal, i.e., the equal area construction.

Alternatively, split up the integration interval into A to D and D to F:

$$P(V_F - V_D) + P(V_D - V_B) = \int_{\tilde{V}_B}^{\tilde{V}_D} d\tilde{V} P(\tilde{V}, T) + \int_{\tilde{V}_D}^{\tilde{V}_F} d\tilde{V} P(\tilde{V}, T).$$

which can be rewritten to

$$0 = \int_{\tilde{V}_B}^{\tilde{V}_D} d\tilde{V} [P(\tilde{V}, T) - P] + \int_{\tilde{V}_D}^{\tilde{V}_F} d\tilde{V} [P(\tilde{V}, T) - P].$$

or

$$\int_{\tilde{V}_B}^{\tilde{V}_D} d\tilde{V} [P - P(\tilde{V}, T)] = \int_{\tilde{V}_D}^{\tilde{V}_F} d\tilde{V} [P(\tilde{V}, T) - P].$$

The left hand side is the area enclosed by BCDB, while the right hand side is the area enclosed by DEFD, i.e., the equal area construction.

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