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Übungen zu Zeitabhängige Phänomene
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Übungsblatt 8: Linear response theory

The Liouville operator The time evolution of the phase space probability density $f(\mathbf{r}^N, \mathbf{p}^N, t)$ is given by the Liouville equation. The Liouville equation is the $6N$-dimensional equation of continuity of an incompressible fluid of points in phase space which can be neither created nor destroyed. It can be written in compact form using the Poisson bracket notation

$$\frac{\partial f}{\partial t} = \{\mathcal{H}, f\},$$

where $\mathcal{H}$ is Hamilton's function and the Poisson bracket of two phase space functions A and B is given by

$$\{A, B\} = \sum_{i=1}^{N} \left(\frac{\partial A}{\partial \mathbf{r}_i} \cdot \frac{\partial B}{\partial \mathbf{p}_i} - \frac{\partial A}{\partial \mathbf{p}_i} \cdot \frac{\partial B}{\partial \mathbf{r}_i} \right).$$

By defining the Liouville operator $\mathcal{L} = i\{\mathcal{H}, \ \}$ find a formal solution to the Liouville equation in terms of $\mathcal{L}$. Consider a general function of the phase space coordinates $A(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{p}_1, \mathbf{p}_2, \cdots)$. Express the total differential $\frac{dA}{dt}$ in terms of the partial derivatives of A with respect to the $\mathbf{r}_i$ and $\mathbf{p}_i$. Use Hamilton's equations to show that A obeys an equation very similar to the Liouville equation for the distribution function and show that the formal solution for the time evolution is given by $A(t) = \exp(i\mathcal{L}t)A(0)$.

Correlation functions The dynamic properties of many particle systems are conveniently described in terms of their time correlation functions. In this problem we will obtain some useful general properties of correlation functions. The time correlation function between two dynamical variables $A(t) \equiv A(\mathbf{r}^N(t), \mathbf{p}^N(t))$ and $B(t) \equiv B(\mathbf{r}^N(t), \mathbf{p}^N(t))$ is written as $C_{BA}(t', t'') = \langle A(t')B(t'')\rangle$. Show that $\exp(i\mathcal{L}t)A(\mathbf{r}^N, \mathbf{p}^N) = A(\mathbf{r}^N(t), \mathbf{p}^N(t))$ for Liouville dynamics. The average $\langle\,\rangle$ denotes either an ensemble average over initial conditions or a time averages. Comment on the assumption that time and ensemble averages are equivilent. Under what conditions might this not be the case? Show that an ensemble average can be written as

$$\langle A(t')B(t'')\rangle = \int d\Gamma\, f_0 B(t'') \exp(-\mathcal{L}(t' - t''))A(t''),$$

where the Liouville operator acts to the right. Write the corresponding expression for the time average. Because the canonical equilibrium distribution $f_0 \propto \exp(-\beta\mathcal{H}_0)$ is independent of time the correlation function becomes a function of only the time difference $t = t' - t''$, $C_{AB}(t) = \langle A(t)B(0)\rangle$. This property is called stationarity. Show that stationarity implies the following

$$\langle \dot{A}(t)B(0)\rangle = -\langle A(t)\dot{B}(0)\rangle \qquad \frac{d^2}{dt^2}\langle A(t)B(0)\rangle = -\langle \dot{A}(t)\dot{B}(0)\rangle.$$

The two relations given above simply express the fact that $\mathcal{L}$ is hermitian with respect to the inner product $\langle A(t')\mathcal{L}B(t'')\rangle$. Integrate by parts to prove that $\mathcal{L}$ is a hermitian operator. Show that the time translational invariance of $C_{AB}(t)$ implies that $C_{AB}(t) = \epsilon_A \epsilon_B C_{AB}(t)$, where ϵ_A and ϵ_B are the time-reversal signatures of the variables A and B. It is generally the case that $\mathcal{H}$ is of even parity under spatial inversion $\mathbf{r}_i, \mathbf{p}_i \to -\mathbf{r}_i, -\mathbf{p}_i$. What does this imply about the parity of the Liouville operator? What is the time correlation function $C_{AB}(t)$ when A and B have opposite parities under spatial inversion?

Of special importance are the autocorrelation functions $C_{AA}(t)$. Comment on how the above results could be used to extract the velocity autocorrelation function in a liquid from observing the particle displacements. In fact the autocorrelation function is generally defined as $C_{AA}(t) = \langle A(t)A^* \rangle$ to ensure that $C_{AA}(t)$ remains real. Use Schwarz's inequality to prove that the correlation function is bounded from above by it's initial value

$$|C_{AA}(t)| \leq C_{AA}(0).$$

Give a physical explanation why this result is to be expected. If we define the dynamical variables in such a way as to remove their average values, $C_{AB}(t) = \langle \delta A(t) \delta B(0) \rangle$, where $\delta A(t) = A(t) - \langle A \rangle$, then we can define the Fourier transform $C_{AB}(\omega)$. The function $C_{AB}(\omega)$ is often called the power spectrum and is important as it provides the connection between correlation functions and numerous experimental measurements. Show that the power spectrum of an autocorrelation function is always a real, even function of ω. By considering the average $\langle A_T(\omega) A_T^*(\omega) \rangle$ with $A_T(\omega) = \int_{-T}^{T} dt \, \exp(i\omega t) A(t)/\sqrt{2T}$ show that the power spectrum of an autocorrelation function is non-negative. Finally, show that the auto correlation function has the following short time expansion

$$C_{AA}(t) = \sum_{n=0}^{\infty} \frac{t^{2n}}{(2n)!} (-1)^n \langle |(i\mathcal{L})^n A|^2 \rangle$$

and that the frequency moments of the power spectrum are related to derivatives of the $t = 0$ value of the autocorrelation function ('sum rules')

$$\int_{-\infty}^{\infty} d\omega \, \omega^{2n} C_{AA}(\omega) = (-1)^n \left(\frac{d^{(2n)} C_{AA}(t)}{dt^{(2n)}} \right)_{t=0}.$$

Linear response theory We now want to consider the effect upon dynamical variables of small perturbations in the Hamiltonian. When the system is subject to some external influence the Hamiltonian is modified $\mathcal{H} = \mathcal{H}_, + \mathcal{H}'(t)$, where the perturbation is a product of an applied space and time-dependent field $F(\mathbf{r}, t)$ which couples to the dynamical variable $A(\mathbf{r})$, $\mathcal{H}'(t) = -\int d\mathbf{r} A(\mathbf{r}) F(\mathbf{r}, t)$. Using the results of the previous exercise and assuming that the system is in equilibrium for $t \to -\infty$ show that to linear order in $F(\mathbf{r}', t')$ the perturbed distribution function is given by

$$f(t) = f_0 - \int_{-\infty}^{t} dt' \int d\mathbf{r}' \, e^{-i\mathcal{L}_0 (t-t')} \{A(\mathbf{r}'), f(t')\} F(\mathbf{r}', t'),$$

where $\mathcal{L}_0$ is the Liouville operator of the unperturbed Hamiltonian. Using similar arguments show that the mean change in the variable B resulting from the perturbation coupling to variable A is given by

$$\langle \delta B(\mathbf{r}, t) \rangle = \int_{-\infty}^{t} dt' \int d\mathbf{r}' \, \chi_{AB}(\mathbf{r} - \mathbf{r}', t - t') F(\mathbf{r}', t'),$$

where the response function $\chi_{AB}(\mathbf{r} - \mathbf{r}', t - t') = -\{B(\mathbf{r}, t), A(\mathbf{r}', t')\}$ and we have used the hermitian property of the Liouville operator. Note that the response function is non-local in both space and time, where the time non-locality reflects the memory of the system. Using the definition of the time correlation function show that in equilibrium the following relation holds

$$\frac{\partial}{\partial t} C_{AB}(t) = -k_B T \chi_{AB}(t),$$

where $\chi_{AB}(t) = \langle\{f_0, A^*(t)\}B\rangle$. Thus show that the thermodynamic response $\chi^0_{AB} \equiv \int_0^\infty dt\, \chi_{AB}(t)$ is given by $\chi^0_{AB} = \chi^T_{AB}(1 - f_{AB})$, where χ^T_{AB} is the isothermal susceptibility and f_{AB} is the non-ergodicity parameter $f_{AB} = C_{AB}(\infty)/k_BT$.