Seminar on problem solving in physics NFPL087, Tue 15:00

Problem Sheet 6

TOPIC: Autocorrelation functions and spectroscopy

1 **Harmonic oscillator**
Calculate the autocorrelation functions for a classical linear harmonic oscillator in thermodynamic equilibrium at temperature T. The Hamiltonian of the system is $H(p,q) = p^2/(2M) + (M\Omega^2/2)q^2$, where M denotes the mass and Ω denotes the frequency.

(a) Using Boltzmann statistics, evaluate the equilibrium averages $\langle p^2 \rangle$, $\langle pq \rangle$ and $\langle q^2 \rangle$!

(b) Solve the Hamiltonian equations of motion for $p(t)$ and $q(t)$ with $p(0)$ and $q(0)$ as initial conditions; express the $p(t)$ and $q(t)$ in terms of the $p(0)$ and $q(0)$.

(c) In this step, we proceed to an equilibrium ensemble of trajectories in phase space. Each trajectory is parameterized by the $p(0)$ and $q(0)$; the probability of each trajectory is given by the Boltzmann distribution. Calculate the momentum autocorrelation function $\Gamma_{pp}(t) := \langle p(t)p(0) \rangle$. For the average values of the initial conditions, assume equilibrium averages, *i.e.* $\langle p^2(0) \rangle = \langle p^2 \rangle$ and $\langle p(0)q(0) \rangle = \langle pq \rangle$. Hint: the result should be $\Gamma_{pp}(t) = Mk_BT\cos(\Omega t)$.

(d) Introducing the dipole moment, $\mu(t) = Qq(t)$ (Q is the charge of the oscillating particle), calculate the time-dependent dipole-dipole correlation function, $\Gamma_{\mu\mu}(t) := \langle \mu(t)\mu(0) \rangle$.

(e) Calculate the Fourier-transformed dipole-dipole correlation function, given by the formula

$$\Gamma_{\mu\mu}(\omega) = \int_{-\infty}^{\infty} e^{i\omega t}\, \Gamma_{\mu\mu}(t)\mathrm{d}t.$$

The following representation of the delta function comes handy: $\frac{1}{2\pi}\int_{-\infty}^{\infty} e^{i(\omega-\omega')t}\mathrm{d}t = \delta(\omega-\omega')$.

(f) Discussion: the Fourier-transformed correlation function, also called the power spectrum, can be measured by spectroscopies. The present model can apply to molecular vibrations, for example. Discuss, what could one learn about the vibrational mode from the spectrum.

Literature:

– Time-Correlation Function Description of Absorption Lineshape.
Chemistry LibreTexts. (2020, December 12). Retrieved May 6, 2021,
from https://chem.libretexts.org/@go/page/107280

– B.J.Berne, G.D.Harp, On the calculation of time correlation functions, Adv. Chem. Phys. 17 (1970): 63-227.

2 **Coupled linear harmonic oscillators**

Generalize the previous result to a system of classical coupled linear harmonic oscillators at temperature T, consisting of N identical mass points (of mass M) labeled by an index i ($i = 1, 2, \ldots, N$), with dynamics driven by the Hamiltonian

$$H\left(\{p_i\}, \{q_i\}\right) = \frac{1}{2M} \sum_{i=1}^{N} p_i^2 + \frac{1}{2} \sum_{i,j=1}^{N} q_i \Phi_{ij} q_j \,,$$

where Φ_{ij} is a real symmetric positive definite $N \times N$ matrix. For this system, evaluate the momentum autocorrelation function defined by

$$\Gamma_{pp}(t) = \frac{1}{N} \sum_{i=1}^{N} \langle p_i(t) p_i(0) \rangle \,.$$

(a) Consider a canonical transformation to the so-called normal variables P_α and Q_α ($\alpha = 1, 2, \ldots, N$), defined by linear relations $q_i = \sum_\alpha A_{i\alpha} Q_\alpha$ and $p_i = \sum_\alpha A_{i\alpha} P_\alpha$, where $A_{i\alpha}$ is a real orthogonal time-independent $N \times N$ matrix. The transformation can be chosen such that the transformed Hamiltonian describes a system of independent linear harmonic oscillators with frequencies Ω_α,

$$H\left(\{P_\alpha\}, \{Q_\alpha\}\right) = \sum_{\alpha=1}^{N} \left(\frac{1}{2M} P_\alpha^2 + \frac{M\Omega_\alpha^2}{2} Q_\alpha^2 \right).$$

(b) Express $\Gamma_{pp}(t)$ through the normal variables. Reminder: $\sum_i A_{i\alpha} A_{i\alpha'} = \delta_{\alpha\alpha'}$. You should obtain the sum of independent oscillator terms, for which the result of Problem **1** can be used.
Result: $\Gamma_{pp}(t) = M k_B T \, (1/N) \sum_{\alpha=1}^{N} \cos(\Omega_\alpha t)$.

(c) **Linear chain.** Apply the previous formula to a linear chain of identical masses coupled by equal strings. Instead of the label α, label the normal modes by the wavenumber k. In the infinite (*aka* thermodynamic) limit $N \to \infty$, replace the sum by an integral, $\frac{1}{N} \sum_k \mapsto \frac{a}{2\pi} \int_{-\pi/a}^{+\pi/a} \mathrm{d}k$. The lattice parameter is denoted by a.

(d) **Debye approximation.** Hereby, the integral can be simplified in the Debye approximation, $\Omega(k) = v|k|$, where v is the sound velocity. Remind yourself of the exact dispersion law for a chain and compare to the Debye approximation. Evaluate the integral and express the autocorrelation function. The product $v \cdot \frac{\pi}{a}$ is the maximal frequency, it is referred to as the Debye frequency, Ω_{D}.

(e) Discussion: Compare the long-time behavior of $\Gamma_{pp}(t)$ of a finite number of oscillators with the infinite chain. What is the fundamental difference in the long-time limit? Imagine a heavy particle (mass $m \gg M$) that is coupled to a system of oscillators. Can the particle experience friction / dissipation if the system of oscillators is finite/infinite?

3 **Density-density correlation function and the dynamic structure factor**

The density-density correlation function is defined by the relation $\Gamma_{n(\mathbf{x}_1)n(\mathbf{x}_2)}(t) = \langle n(\mathbf{x}_1, t) n(\mathbf{x}_2, 0) \rangle$, where $n(\mathbf{x}, t)$ is the particle density. The dynamic structure factor is defined by

$$S(\mathbf{k}, \omega) = \int \mathrm{d}t \int \mathrm{d}^3 \mathbf{x}_1 \int \mathrm{d}^3 \mathbf{x}_2 \, e^{i\omega t} e^{-i\mathbf{k}\cdot(\mathbf{x}_1 - \mathbf{x}_2)} \, \Gamma_{n(\mathbf{x}_1)n(\mathbf{x}_2)}(t),$$

i.e. it is a Fourier transformation of the density-density correlation function both in time and space. This quantity can be measured by various probes, such as inelastic neutron scattering or Raman spectroscopy. In this problem, you will calculate the dynamic structure factor of a harmonic oscillator.

(a) By performing both spatial integrals, show that $S(\mathbf{k}, \omega) = \int dt\, e^{i\omega t} \langle n(\mathbf{k}, t) n(-\mathbf{k}, 0) \rangle$, where $n(\mathbf{k}, t) = \int d^3\mathbf{x}\, e^{-i\mathbf{k}\cdot\mathbf{x}} n(\mathbf{x}, t)$.

(b) In one dimensional problems, the density of a single particle is given by $n(x, t) = \delta(x - q(t))$, where $q(t)$ is the time-dependent coordinate of the particle. Calculate the spatial Fourier transform, $n(k, t)$! (From now we focus on 1D problems only.)

(c) We will consider low momentum transfer (such as when long-wavelength radiation is used). For low k, the exponential in $n(k, t)$ can be expanded to linear order in k. Insert the $q(t)$ for a linear harmonic oscillator from Problem $\boxed{1}$. Evaluate the temporal Fourier transformation to get $S(k, \omega)$. Hint: $\frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i(\omega - \omega')t} dt = \delta(\omega - \omega')$.

Further reading about correlation functions (and spectroscopies) in condensed matter physics:

M. Chaikin, T. C. Lubensky, Principles of Condensed Matter Physics, Cambridge University Press (October 9, 2000)