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Advanced Statistical Physics II – Problem Sheet 2

Problem 1 – **Liouville Operator**

(3P) In the lecture it was shown that the Liouville operator $L(q, p)$ is anti-self adjoint, i.e.

$$\int dq\ dp\ A(q,p)L(q,p)B(q,p) = -\int dq\ dp\ B(q,p)L(q,p)A(q,p). \tag{1}$$

Based on this, prove that

$$\int dq\ dp\ A(q,p)e^{-tL(q,p)}B(q,p) = \int dq\ dp\ B(q,p)e^{tL(q,p)}A(q,p). \tag{2}$$

Comment: If you now choose $B(q, p) = \rho_0(q, p)$, this result can be used to relate the Schrödinger picture to the Heisenberg picture, namely

$$\begin{aligned}\int dq\ dp\ A(q,p)e^{-tL(q,p)}\rho_0(q,p) &= \int dq\ dp\ A(q,p)\rho(q,p,t)\\ &= \int dq\ dp\ \rho_0(q,p)e^{tL(q,p)}A(q,p)\\ &= \int dq\ dp\ \rho_0(q,p)A(q,p,t).\end{aligned}$$

Problem 2 – **Kolmogorov Theorem**

(3P) In the lecture we proved the Kolmogorov theorem

$$\int dqdp\ \rho(q',p',t+\tau;q,p,t) = \rho(q',p',t+\tau), \tag{3}$$

by using Bayes' theorem

$$\rho(q',p',t+\tau;q,p,t) = \rho(q',p',t+\tau|q,p,t)\rho(q,p,t) \tag{4}$$

and explicit expressions for $\rho(q', p', t+\tau|q, p, t)$ and $\rho(q, p, t)$ based on solutions of the Liouville equation.
Here prove the alternative formulation of the Kolmogorov theorem

$$\int dq'dp' \ \rho(q', p', t+\tau; q, p, t) = \rho(q, p, t). \tag{5}$$

Problem 3 – **Energy Conservation**

The balance equation for the internal energy density $u(\vec{r}, t)$ of a closed system with fixed volume and mass density $\rho(\vec{r}, t)$ with local velocity $\vec{v}(\vec{r}, t)$ is given by

$$\frac{\partial}{\partial t}\left[\rho(\vec{r}, t)u(\vec{r}, t)\right] + \nabla_j[v_j(\vec{r}, t)\rho(\vec{r}, t)u(\vec{r}, t) + J_j^q(\vec{r}, t)] = M(\vec{r}, t). \tag{6}$$

Here $\vec{J}^q(\vec{r}, t)$ is the conductive heat flux and $\vec{v}(\vec{r}, t)\rho(\vec{r}, t)u(\vec{r}, t)$ the convective flux. $M(\vec{r}, t)$ is an arbitrary source of internal energy, for example a heat source.

a) (2P) Reformulate the conservation law using the convective derivative

$$\frac{d}{dt} = \frac{\partial}{\partial t} + v_j(\vec{r}, t) \ \nabla_j, \tag{7}$$

and conservation of mass

$$\frac{\partial \rho}{\partial t} = -\nabla_j(v_j\rho) \tag{8}$$

to arrive at an equation for du/dt.
b) (2P) Use the specific heat capacity c_v

$$\frac{du}{dt} = c_v\frac{\partial T}{\partial t}, \tag{9}$$

and the Fourier law

$$J_j^q = -\alpha\nabla_j T, \tag{10}$$

where α is the thermal conductivity to obtain a differential equation for the temperature, also known as the heat equation. Assume there are no sources of internal energy.
c) (2P) Give a solution for stationary temperature profile of a one-dimensional water pipe of length L with temperatures T_0 and T_L at the boundaries and no sources of internal energy.

Problem 4 – **Linear Response**

a) (2P) Write down the Hamiltonian for a single dipole $\vec{p}(t)$ in 3 dimensions, for example a water molecule whose orientation is perturbed by an external electric field in z-direction $E_0(t)$.
b) (3P) Assuming the correlation function for the polarization of a single molecule is given by a single exponential $\langle \vec{p}(t)\vec{p}(0)\rangle = p_0^2 \exp(-t/\tau)$, compute the time-dependent expectation value of the polarization produced by a constant external field $\vec{E}_0$, switched on at time $t = 0$.
c) (3P) Compute the response function of the polarization in Fourier space $\tilde{\chi}_{pp}(\omega)$, which is related to the absorption spectrum measured in experiments. Use your result to identify the fit function used in the plot of the dielectric spectrum of water shown below.
Hint: Split the result into real and imaginary part.

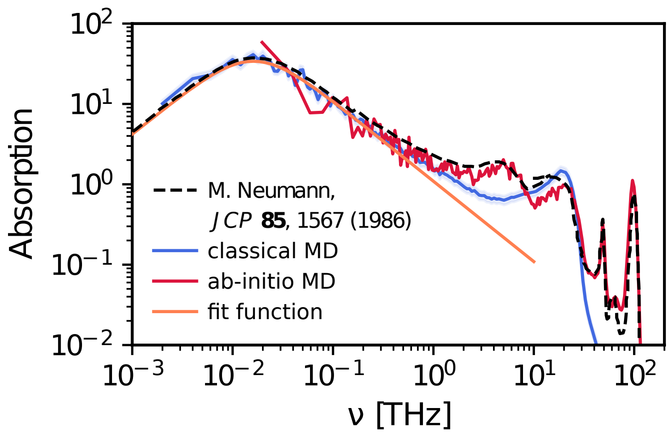

Figure 1: Absorption spectrum of water determined from experiment as well as classical and quantum-mechanical MD simulations. The fit function is the so-called Debye function.