Chemistry 276 - Autumn 2009-10 - Advanced Physical Chemistry
Problem Set 3

Due in class on 10/15/09.

In the analysis of many typical problems in statistical mechanics, it is common to express some quantity of interest in terms of static averages or dynamic correlation functions of equilibrium systems. These quantities have many general properties in common, and it is worthwhile understanding these properties and their relationships.

In the following notes and exercises, we focus on these general properties for canonical ensemble averages for an equilibrium system with a time independent Hamiltonian. The background for much of what we have to discuss is in Lecture Notes 6 and 8 that are posted. Here we shall review some of the definitions and discuss the consequences.

1 Definitions

Phase space. Let Γ correspond to a point in phase space for a system of interest.

Hamiltonian. The Hamiltonian $H(\Gamma)$ is a function of Γ.

Canonical distribution function. The equilibrium canonical ensemble distribution function is

$$P_{eq}(\Gamma) \propto \exp\left(-H(\Gamma)/k_B T\right)$$

The normalized version is

$$P_{eq}(\Gamma) = \frac{\exp\left(-H(\Gamma)/k_B T\right)}{\int d\Gamma' \exp\left(-H(\Gamma')/k_B T\right)}$$

Dynamical variables. A dynamical variable $A(\Gamma)$ is a function of Γ. Many measureable properties of a physical system are dynamical variables.

Equilibrium averages of dynamical variables (static averages). If A is a dynamical variable, then its equilibrium average is

$$\langle A \rangle \equiv \int d\Gamma \, P_{eq}(\Gamma) A(\Gamma)$$

It is the average of $A(\Gamma)$ over the equilibrium distribution of states Γ. (Such quantities are sometimes referred to as 'static averages' since there is no apparent reference to time and since the properties of the equilibrium system do not depend on time.)

Comment. The ensemble postulate asserts that this average is equal to the experimental value of A if measured at time 0 for an equilibrium system.

Dynamics. Let $\gamma(t; \Gamma, t')$ be the location in phase space at time t of the point that was at Γ at time t'. $\gamma(t; \Gamma, t')$ is in principle calculated by starting a system at Γ at time t' and integrating the equations of motion for the coordinates and momenta forward in time until time t.

If the Hamiltonian is independent of time, $\gamma(t; \Gamma, t')$ in fact depends only on $t - t'$. Only the time interval and the starting point are relevant for solving the differential equations when the Hamiltonian is independent of time. Thus we have

$$\gamma(t; \Gamma, t') = \gamma(t - t'; \Gamma, 0)$$

Time dependent dynamical variables. If A denotes a physical quantity and $A(\Gamma)$ is the function associated with it, then $A(t, \Gamma)$ denotes the corresponding time dependent dynamic variable. $A(\Gamma)$ is the value of the physical quantity A when the state is Γ. $A(t, \Gamma)$ is the value of the physical quantity A at time t when the state of the system was Γ at time t_0.

Note that

$$A(t_0, \Gamma) = A(\Gamma)$$

To define time dependent dynamical variables in a consistent way, we need to decide on a value of t_0 and use it consistently. Here for simplicity, we choose $t_0 = 0$.

Averages of time dependent dynamical variables. The average of a time dependent dynamical variable is

$$\langle A(t)\rangle \equiv \int d\Gamma\, P_{eq}(\Gamma)A(\Gamma,t)$$

It is the average, over a canonical ensemble formed at time t_0, of the property A evaluated at time t.

Theorem. $\langle A(t)\rangle = \langle A\rangle$.

Comment. Such averages are independent of time. The ensemble postulate of equilibrium statistical mechanics implies that $\langle A(t)\rangle$ should be equal to the measured value of A at time t for a system that was at equilibrium at time 0. Thus we expect the result to be independent of time.[1]

Average of the product of two time dependent dynamical variables.

$$\langle A(t_1)B(t_2)\rangle \equiv \int d\Gamma\, A(t_1,\Gamma)B(t_2,\Gamma)P_{eq}(\Gamma)$$

Comment. This can be given a complicated interpretation in terms of the ensemble postulate, but the interpretation is largely irrelevant. The importance of such quantities is that they arise in theoretical analyses of various experiments.

Theorem. $\langle A(t_1)B(t_2)\rangle$ depends only on the time interval $t_1 - t_2$. [2]

Time correlation functions.

$$C_{AB}(t_1 - t_2) \equiv \langle A(t_1)B(t_2)\rangle$$

This is called the correlation function of A and B. If the two dynamical variables are the same, e.g. A and A, the function is called an 'autocorrelation function'.

[1] We proved this in lecture.
[2] We proved this in lecture.

2 Exercises

Prove the following statements for arbitrary real dynamical variables A and B starting from the definitions and theorems in section 1. (Most of them are trivial. The purpose of this is just to get you used to manipulating these functions.)

1. $C_{AB}(t) = C_{BA}(-t)$. (A correlation function value is unchanged if the subscripts are switched and the sign of the time is changed.)
2. $C_{AB}(0) = \langle AB \rangle$. (A zero time correlation function is equal to a static average.)
3. $C_{AB}(0) = C_{BA}(0)$. (For zero time, the value of a time correlation function is symmetric under interchange of the subscripts.)

   Additional question: can $C_{AB}(0)$ be equal to zero? If so, give an example.
4. $C_{AA}(0) \geq 0$. (For zero time, an autocorrelation function of real variables is nonnegative.)

   Additional question: can $C_{AA}(0)$ be equal to zero? If so, give an example.
5. $C_{AA}(t) = C_{AA}(-t)$. An autocorrelation function of a real variable is even in time.

3 More definitions

Fluctuation of a dynamical variable from its average. If $A(\Gamma)$ is a dynamical variable, then its fluctuation its defined as

$$\delta A(\Gamma) = A(\Gamma) - \langle A \rangle$$

Time derivative of a dynamical variable. If $A(\Gamma)$ is a dynamical variable, its time derivative is also a dynamical variable. This follows because if the phase point of a system is at Γ at a certain time and the phase point is moving according to Hamilton's equations, the time derivative of A at that time is

$$\sum_{i\alpha}\left(\frac{\partial A(\Gamma)}{\partial Q_{i\alpha}}\dot{Q}_{i\alpha}+\frac{\partial A(\Gamma)}{\partial P_{i\alpha}}\dot{P}_{i\alpha}\right)$$

where the sum is over all the degree of freedom of the system and the time derivatives are to be evaluated at the time that the system is at Γ. It follows from Hamilton's equations that this is equal to

$$\sum_{i\alpha}\left(\frac{\partial A(\Gamma)}{\partial Q_{i\alpha}}\frac{\partial H(\Gamma)}{\partial P_{i\alpha}}-\frac{\partial A(\Gamma)}{\partial P_{i\alpha}}\frac{\partial H(\Gamma)}{\partial Q_{i\alpha}}\right)$$

This is clearly just a function of Γ and not of time or anything else, which shows that it indeed is a dynamical variables. We define

$$\dot{A}(\Gamma)\equiv\sum_{i\alpha}\left(\frac{\partial A(\Gamma)}{\partial Q_{i\alpha}}\frac{\partial H(\Gamma)}{\partial P_{i\alpha}}-\frac{\partial A(\Gamma)}{\partial P_{i\alpha}}\frac{\partial H(\Gamma)}{\partial Q_{i\alpha}}\right)$$

The physical meaning of this is clear. It is the time derivative of A when the system is at Γ.

4 More exercises

1. Find the value of $\langle\dot{A}\rangle$.
2. Find the relationship between $\dot{A}$, $\dot{\delta A}$, and $\delta\dot{A}$. (Here $\dot{\delta A}$ means the time derivative of δA and that $\delta\dot{A}$ means the fluctuation of $\dot{A}$ from its ensemble average.)
3. Find the relationships among the following functions: $C_{AB}(t)$, $C_{\delta A,B}(t)$, $C_{A,\delta B}(t)$, and $C_{\delta A,\delta B}(t)$.
4. Find the relationships among the following functions: $C_{AB}(t)$, $C_{A\dot{B}}(t)$, $C_{\dot{A}B}(t)$, $C_{\delta A,\delta\dot{B}}(t)$, $C_{\delta\dot{A},\delta B}(t)$.
5. Each of the following can be expressed simply in terms of a static average. Find the expressions for each of the following:
   (a) $C_{AB}(0)$
   (b) $(d/dt)C_{AB}(t)|_{t=0}$.

(c) $(d^2/dt^2)C_{AB}(t)|_{t=0}$

(d) $C_{\dot{A}B}(0)$

(e) $(d/dt)C_{\dot{A}B}(t)|_{t=0}$