Classical and Statistical mechancis

Home Work # 3
Posted on November 8, 2018
Due in Class November 20, 2018

1. *Canonical Transformations Example 1*

   a) From the theory of canonical transformations calculate the transformation generated by $F_1(q, Q) = Q/q$ of the free particle problem

   $$H = p^2/(2m).$$

   b) Find the Hamiltonian equations of motion in the new representation, and solve them exactly.

2. *Canonical Transformations Example 2*

   a) Show that a canonical transformation from q, p to any required $Q \equiv Q(q)$ (i.e. a function of q only) can be generated by the generator $F_2(q, P)$.

   b) Find the $F_2(q, P)$ necessary to make the transformation in 2 dimensions from $\vec{r} = \{x, y\}$ to the standard polar coordinates r, θ .

   c) Using (b) find the full transformation from $\vec{q}, \vec{p}$ to the new canonical momenta and coordinates.

   d) Verify that the new coordinates satisfy the canonical algebra by computing the 4 poisson brackets $\{Q_i, P_j\}_{q,p}$.

3. *Action problem*

   a) For the simple harmonic oscillator

   $$H = p^2/(2m) + kq^2/2,$$

   calculate the action

   $$J(E) = \oint p dq,$$

   by integrating over a complete cycle. From the derivative with respect to energy, calculate the time period.

b) Do the same calculation for the quartic oscillator

$$H = p^2/(2m) + kq^4/4,$$

where you can use scaling to get the energy dependence of the action, and ignore (i.e. leave undetermined) the fairly cumbersome integral, which is dimensionless and hence less important.

c) Show that time period can be written as

$$T(E) = \int \int dp\, dq\, \delta(H - E),$$

by differentiating the formula for $J(E)$ and evaluate this integral for the Harmonic oscillator directly to confirm the result of (a).

{ Hint: This problem requires you to use the familiar formulat $\delta(x) = \frac{d}{dx}\Theta(x)$ where Θ is the Heaviside step function. }

4. *Thermodynamics and partial derivatives Example 1*

a) We worked out a few examples of thermodynamic potentials,

$$dE = T\, dS - p\, dV + \mu\, dN$$
$$dF = -S\, dT - p\, dV + \mu\, dN$$
$$d\Omega = -S\, dT - p\, dV - N\, d\mu$$

Using the standard conditions for exact differentials, this leads to the Maxwell relations. For example from the first equation we read

$$\frac{\partial^2 E}{\partial S \partial V} = \frac{\partial^2 E}{\partial V \partial S}$$

and hence

$$-\frac{\partial p}{\partial S}\Big|_{V,N} = \frac{\partial T}{\partial V}\Big|_{S,N}.$$

This is an example of a Maxwell relation. It is infact rather useless since we did not choose the potential strategically. We get more useful ones by rewriting the first equation by moving S to one side and everything else to the other. Doing this, write down the 3 Maxwell relations from the first equation.

b) Similarly write down the 4 Maxwell relations from the second and third potentials by dropping the number variation.

5. *Thermodynamics and partial derivatives Example 2*

   Using the tricks in Landau Lifshitz Stat Mech (Pages 49-51 - scan in the website) show

   a)
   $$\frac{\partial C_p}{\partial P}\Big|_T = -T\frac{\partial^2 V}{\partial T^2}\Big|_P$$

   This is Eq 16.2 of LL.

   b) Show that (16.6)

   $$\frac{\partial E}{\partial P}\Big|_T = -T\frac{\partial V}{\partial T}\Big|_P - P\frac{\partial V}{\partial P}\Big|_T$$

   c)Show that (16.8-1)

   $$\frac{\partial E}{\partial T}\Big|_P = C_p - P\frac{\partial V}{\partial T}\Big|_P$$

6. *No submission required but verify these important identities for Jacobians*

   Page 51 LL, (I), (II), (III), (IV), (V).

   {We will use these in the next few classes }

Correspondingly, in a state of thermal equilibrium the free energy and the thermodynamic potential have minimum values, the former with respect to all changes of state with T and V constant, and the latter with respect to changes of state with T and P constant.

PROBLEM

How can the mean kinetic energy of the particles in a body be calculated if the formula for its free energy is known?

SOLUTION. The Hamiltonian function (or, in the quantum case, the Hamiltonian operator) may be written in the form $E(p, q) = U(q) + K(p)$, where $U(q)$ is the potential energy of interaction of the particles in the body, and $K(p)$ their kinetic energy. The latter is a quadratic function of the momenta, inversely proportional to the particle mass m (for a body consisting of identical particles). Regarding m as a parameter, we can therefore write

$$\frac{\partial E(p, q; m)}{\partial m} = -\frac{1}{m} K(p).$$

Then, applying formula (15.11), we obtain the mean kinetic energy $K = \overline{K(p)}$:

$$K = -m(\partial F/\partial m)_{T, V}.$$

§16. Relations between the derivatives of thermodynamic quantities

In practice the most convenient, and the most widely used, pairs of thermodynamic variables are T, V and T, P. It is therefore necessary to transform various derivatives of the thermodynamic quantities with respect to one another to different variables, both dependent and independent.

If V and T are used as independent variables, the results of the transformation can be conveniently expressed in terms of the pressure P and the specific heat C_v (as functions of V and T). The equation which relates the pressure, volume and temperature is called the *equation of state* for a given body. Thus the purpose of the formulae in this case is to make it possible to calculate various derivatives of thermodynamic quantities from the equation of state and the specific heat C_v.

Similarly, when P and T are taken as the basic variables the results of the transformation should be expressed in terms of V and C_p (as functions of P and T).

Here it must be remembered that the dependence of C_v on V or of C_p on P (but not on the temperature) can itself be determined from the equation of state. It is easily seen that the derivative $(\partial C_v/\partial V)_T$ can be transformed so that it is defined in terms of the function $P(V, T)$. Using the fact that $S = -(\partial F/\partial T)_V$, we have

$$\left(\frac{\partial C_v}{\partial V}\right)_T = T\frac{\partial^2 S}{\partial V \partial T} = -T\frac{\partial^3 F}{\partial V \partial T^2}$$

$$= -T\frac{\partial^2}{\partial T^2}\left(\frac{\partial F}{\partial V}\right)_T,$$

and since $(\partial F/\partial V)_T = -P$, we have the required formula

$$(\partial C_v/\partial V)_T = T(\partial^2 P/\partial T^2)_V.$$ (16.1)

Similarly we find

$$(\partial C_p/\partial P)_T = -T(\partial^2 V/\partial T^2)_P,$$ (16.2)

formulae (15.8) being used in the calculation.

We shall show how some of the thermodynamic derivatives most often encountered may be transformed.

The derivatives of the entropy with respect to volume or pressure can be calculated from the equation of state by means of the following formulae, which are a direct consequence of the expressions for the differentials of the thermodynamic quantities. We have

$$\left(\frac{\partial S}{\partial V}\right)_T = -\frac{\partial}{\partial V}\left(\frac{\partial F}{\partial T}\right)_V = -\frac{\partial}{\partial T}\left(\frac{\partial F}{\partial V}\right)_T$$

or

$$(\partial S/\partial V)_T = (\partial P/\partial T)_V.$$ (16.3)

Similarly

$$\left(\frac{\partial S}{\partial P}\right)_T = -\frac{\partial}{\partial P}\left(\frac{\partial \Phi}{\partial T}\right)_P = -\frac{\partial}{\partial T}\left(\frac{\partial \Phi}{\partial P}\right)_T$$

or

$$(\partial S/\partial P)_T = -(\partial V/\partial T)_P.$$ (16.4)

The derivative $(\partial E/\partial V)_T$ is calculated from the equation $dE = T\,dS - P\,dV$ as

$$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P$$

or, substituting (16.3),

$$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P.$$ (16.5)

Similarly we can derive

$$\left(\frac{\partial E}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P - P\left(\frac{\partial V}{\partial P}\right)_T,$$ (16.6)

$$\left(\frac{\partial W}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V + V\left(\frac{\partial P}{\partial V}\right)_T, \quad \left(\frac{\partial W}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P, \quad (16.7)$$

$$\left(\frac{\partial E}{\partial T}\right)_P = C_p - P\left(\frac{\partial V}{\partial T}\right)_P, \quad \left(\frac{\partial W}{\partial T}\right)_V = C_v + V\left(\frac{\partial P}{\partial T}\right)_V. \quad (16.8)$$

Finally, we shall show how the specific heat C_v may be calculated from the specific heat C_p and the equation of state, using T and P as the basic variables. Since $C_v = T(\partial S/\partial T)_V$, we have to transform the derivative

$(\partial S/\partial T)_V$ to different independent variables. A transformation of this type is most simply effected by the use of Jacobians.[†] We write

$$C_v = T(\partial S/\partial T)_V$$
$$= T\partial(S, V)/\partial(T, V)$$
$$= T\frac{\partial(S, V)/\partial(T, P)}{\partial(T, V)/\partial(T, P)}$$
$$= T\frac{(\partial S/\partial T)_P (\partial V/\partial P)_T - (\partial S/\partial P)_T (\partial V/\partial T)_P}{(\partial V/\partial P)_T}$$
$$= C_p - T\frac{(\partial S/\partial P)_T (\partial V/\partial T)_P}{(\partial V/\partial P)_T}.$$

Substituting (16.4), we obtain the required formula:

$$C_p - C_v = -T[(\partial V/\partial T)_P]^2/(\partial V/\partial P)_T. \qquad (16.9)$$

Similarly, transforming $C_p = T(\partial S/\partial T)_P$ to the variables T, V, we can derive the formula

$$C_p - C_v = -T[(\partial P/\partial T)_V]^2/(\partial P/\partial V)_T. \qquad (16.10)$$

The derivative $(\partial P/\partial V)_T$ is negative: in an isothermal expansion of a body, its pressure always decreases. This will be rigorously proved in §21. It therefore follows from (16.10) that for all bodies

$$C_p > C_v. \qquad (16.11)$$

In adiabatic expansion (or contraction) of a body its entropy remains constant. The relation between the temperature, volume and pressure of the body in an adiabatic process is therefore determined by various derivatives taken at

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[†] The Jacobian $\partial(u, v)/\partial(x, y)$ is defined as the determinant

$$\frac{\partial(u, v)}{\partial(x, y)} = \begin{vmatrix} \partial u/\partial x & \partial u/\partial y \\ \partial v/\partial x & \partial v/\partial y \end{vmatrix}. \qquad (I)$$

It clearly has the following properties:

$$\frac{\partial(v, u)}{\partial(x, y)} = -\frac{\partial(u, v)}{\partial(x, y)}, \qquad (II)$$

$$\frac{\partial(u, y)}{\partial(x, y)} = \left(\frac{\partial u}{\partial x}\right)_y. \qquad (III)$$

The following relations also hold:

$$\frac{\partial(u, v)}{\partial(x, y)} = \frac{\partial(u, v)}{\partial(t, s)} \cdot \frac{\partial(t, s)}{\partial(x, y)}, \qquad (IV)$$

$$\frac{d}{dt}\frac{\partial(u, v)}{\partial(x, y)} = \frac{\partial(du/dt, v)}{\partial(x, y)} + \frac{\partial(u, dv/dt)}{\partial(x, y)}. \qquad (V)$$