HW 1 Solution Revised on Feb 14 after grading (with comments to your answers)

This time the basic grading scheme is 'meaningful but wrong answer or approach" -5; no solution -10; careless but grave error -3. [As I told you, I do not with to use HW as a grading device; if you wish the contrary, I can be infinitely harsh.] Since I am a capricious grader, if there is something impressive, I will give you an extra credit.

1. The fundamental thermodynamic equation of state for a substance is a relation between entropy S and the thermodynamic coordinates, E (internal energy) and work coordinates such as volume V and magnetization M, and number of particles N. Find at least three relations from the five candidates below that violate some of the fundamental principles of thermodynamics and state why they are not realizable as the equations of state for stable substances. All the Greek letters denote positive constants.

(a) $S = \alpha (NVE^2)^{1/4}$, (b) $S = \alpha (EV)^{1/2} e^{-\gamma V/N}$, (c) $S = \alpha V^2/E$, (d) $S = \alpha E \log(EV/N^2)$, (e) $S = \alpha V \log(EV/N)$.

Solution

There were people who responded sensitively to the word 'stable.' Initially, I put this to avoid negative pressure and negative temperature, at least. A couple of people checked the convexity of -S. Actually, all the examples are thermodynamically problematic (in more than one ways; I mention only the easiest answers). [Good choices with bad reasons are not counted as good answers, although to sense something fishy without any explicit reason is an important ability.] Since $dS = (1/T)dE + (P/T)dV - (\mu/T)dN$, the partial derivatives of S wrt E and V must all be positive. S must be extensive and should vanish in the $T \to 0$ limit. Some people suggest that in the $N \to \infty$ limit under e.g., constant V is strange. However, this is not a very good argument, because E and V are extensive quantities, so if $N \to \infty$, they also should diverge.

(a) passes simple tests. $1/T = (1/2)(NV/E^2)^{1/4}$, so under bounded N, V condition, $T \to 0$ is equivalent to $E \to 0$ (reasonable). Consequently, the third law is satisfied. However, the second order Jacobian is not with a definite sign, so it is not stable.

(b) Its derivative wrt V under constant E and N reads

$$\frac{P}{T} = \alpha E^{1/2} \left[\frac{1}{2\sqrt{V}} - \gamma \frac{\sqrt{V}}{N} \right] e^{-\gamma V/N}$$

This can be negative for large V.

(c) Its derivative wrt E under constant V and N reads

$$\frac{1}{T} = -\alpha V^2 / E^2 < 0$$

(d) We get

$$dS = \alpha \left[\log \frac{EV}{N^2} + 1 \right] dE + \alpha \frac{E}{V} dV - 2\alpha \frac{E}{N} dN$$

This is delicate, but T < 0 is possible.

(e) This violates the fourth law, because the factor in the log is not intensive.

2. [Probability fun problems]

(1) [Monty Hall Problem] There are three boxes, A, B, C, of which one contains a prize. The player is asked to choose one box. Then, Monty opens one of the empty boxes and asks the player whether she would switch the choice. Should the player switch the box? (This is an extremely famous problem, so you can find the answer somewhere (say Wikipedia). You may copy it, if you understand it, but respect the copyright.)¹

(2) There are two kittens. At least one of them is a male. What is the probability that the other kitten is a male? What is the probability that the other kitten is a female? (Assume that the sex ratio of kittens is 1 to 1.)

Solutions

(1) If you are interested in related problems, see Jason Rosenhouse, *The Monty Hall Problem* (Oxford, 2009). Before the intervention of Monty, your success probability is obviously 1/3. After the intervention, you know that the prize is not in the opened box, so the success rate of the not-chosen-closed box is 2/3, because you know that the probability for the remaining two boxes should contain the prize is 2/3, and now that probability is 'concentrated to' the remaining box! You should switch, and your success chance doubles. In the case with 10,000 boxes, the success probability jumps from 0.0001 to 0.9999! Definitely you should switch.

(2) All the cases of two kittens are: (m, m), (m, f), (f, m), (f, f). Kittens are certainly distinguishable. Now, you know one kitten is male, so you have chosen one of the three cases of (m, m), (m, f), (f, m). Hence, the other kitten is male only if you choose (m, m). The probability is 1/3.

3. There is a *d*-dimensional (classical) ideal gas consisting of N particles whose (one-particle) energy-momentum relation reads $\epsilon = c |\mathbf{p}|^{\alpha}$, where α and c are positive constants. Find the equation of state (i.e, PVE relation), C_V (the constant volume heat capacity) and C_P (the constant pressure heat capacity). Use dimensional analysis and avoid any integration.

Solutions

There were couple of people who hostly computed the canonical partition function with the aid of the Γ -function. Although it is a good exercise, the point here is that without calculation you can almost get everything you wish to know macroscopically. [Even in the actual detailed calculation it is a good habit to check the explicit result dimensional analytically.]

The dimension of energy in terms of momentum is $[E] = [p]^{\alpha}$, so the length scale we can construct from this is (following de Broglie) $h/[p] = h/[E]^{(1/\alpha)}$. Therefore, $V(E^{(1/\alpha)}/h)^d$ is dimensionless. This implies that

$$w(E,V) \propto \left[V(E^{(1/\alpha)}/h)^d \right]^N$$
.

Strictly speaking, dimensional analysis alone cannot say this, because both sides are dimensionless; V must appear in the numerator, because S must be an increasing function of V, generally speaking for gases. Therefore, we can write

$$S(E, V) = Nk_B \left[\log V + \frac{d}{\alpha} \log E + c_N \right]$$
$$= Nk_B \left[\log \frac{V}{N} + \frac{d}{\alpha} \log \frac{E}{N} + c \right].$$

¹If you feel the answer not very intuitively acceptable, think of the 10 thousand box case. After you choose one box, Monty opens all but one remaining boxes. What will you do sensibly?

This implies

$$1/T = \frac{\partial S}{\partial E}\Big|_{V} = (d/\alpha)Nk_{B}/E$$
$$P/T = \frac{\partial S}{\partial V}\Big|_{E} = Nk_{B}/V.$$

Thus, $E = (d/\alpha)Nk_BT$, $PV = Nk_BT$, so $PV = (\alpha/d)E$. $C_V = (d/\alpha)Nk_B$.

The easiest way to compute C_P is to use its definition $(\partial H/\partial T)_P = C_P$, where H is the enthalpy of the gas, $H = E + PV = E + Nk_BT$. Hence, $C_P = C_V + Nk_B$, a famous formula. As discussed in a class, (1) may be obtained with the aid of the equipartition of en-

ergy and a general property of homogeneous functions (Euler's theorem). Since the system Hamiltonian is $H = \sum c_i |\mathbf{p}|^{\alpha}$, it is a homogeneous function of degree α . Therefore,

$$\sum_{i} p_i \frac{\partial H}{\partial p_i} = \alpha H,$$

where the summation is over all the components of the momenta of all the particles. This and the equipartition of energy imply

$$\sum_{i} \left\langle p_i \frac{\partial H}{\partial p_i} \right\rangle = N dk_B T = \alpha \langle H \rangle = E.$$

Here, Nd comes from the total number of variables.

There was one answer with the aid of the elementary kinetic theory:

$$P = 2\left\langle \sum \boldsymbol{p}_i \cdot \boldsymbol{v}_i \right\rangle$$

where $\boldsymbol{v} = \partial E / \partial \boldsymbol{p} = \alpha \boldsymbol{p} |\boldsymbol{p}|^{\alpha-2}$. Here, the velocity must be correctly identified (it is not proportional to \boldsymbol{p} ; this is true only when $\alpha = 2$).

4. Demonstrate that Maxwell's relation can always be written in the following form:²

$$\frac{\partial(X,x)}{\partial(y,Y)} = 1.$$

Solution

A very elementary derivation is to start from Young's theorem applied to E:

$$\frac{\partial x}{\partial Y}\Big|_{X} = \frac{\partial y}{\partial X}\Big|_{Y} \Rightarrow \frac{\partial (x,X)}{\partial (Y,X)} = -\frac{\partial (Y,y)}{\partial (Y,X)} \Rightarrow \frac{\partial (x,X)}{\partial (Y,y)} = -\frac{\partial (Y,X)}{\partial (Y,X)} = 1.$$

However, this derivation does not tell us anything about the meaning of the relation. We know

$$dE = \dots + xdX + ydY + \dots,$$

so, as a differential form, $d^2E = 0$; Notice that $d^2E = 0$ implies Young's theorem that $\partial^2 E/\partial a \partial b = \partial^2 E/\partial b \partial a$. That is, if we change x, X, y and Y only

$$dX \wedge dx = -dY \wedge dy.$$

²One way is to check all the possible cases. Is there a better way? [This is not required.]

You could imagine this as a relation between two infinitesimal areas and the Jacobian as their ratio (respecting their orientations; there is -).

If you wish to see that $dX \wedge dx = -dY \wedge dy$ indeed implies Maxwell's relations, you can do the following. For example,

$$dX \wedge \left(\frac{\partial x}{\partial y}\Big|_X dy + \frac{\partial x}{\partial X}\Big|_y dX\right) = \frac{\partial x}{\partial y}\Big|_X dX \wedge dy$$
$$-dY \wedge dy = -\left(\frac{\partial Y}{\partial y}\Big|_X dy + \frac{\partial Y}{\partial X}\Big|_y dX\right) \wedge dy = -\frac{\partial Y}{\partial X}\Big|_y dX \wedge dy$$

Thus, we obtain

$$\left. \frac{\partial x}{\partial y} \right|_X = - \left. \frac{\partial Y}{\partial X} \right|_y.$$

If you start with the formula we wish to check, we can proceed, for example, as follows:

$$\frac{\partial(X,x)}{\partial(x,y)} = \frac{\partial(y,Y)}{\partial(x,y)}$$

This implies

$$\left. \frac{\partial X}{\partial y} \right|_x = \left. \frac{\partial Y}{\partial x} \right|_y$$

Or,

$$\frac{\partial(X,x)}{\partial(Y,x)} = \frac{\partial(y,Y)}{\partial(Y,x)} \quad \Rightarrow \quad \frac{\partial X}{\partial Y}\Big|_x = -\left.\frac{\partial y}{\partial x}\right|_Y$$

etc.

5. What is the sign of

for rubber? You may assume $(\partial S/\partial L)_T < 0$. First, guess your answer with an intuitive explanation.

 $\left. \frac{\partial S}{\partial F} \right|_{L}$

Solution

To increase the force F while keeping the total length L, the chain should move more vigorously, so S should increase. The sign must be positive.

Some people argued as: under constant L, increasing F should increase entropy. In this logic, the causal relation seems opposite. To support this argument some added, increasing F increases the energy of the system, so S should increase. Well, the latter half may be OK, but in our case L does NOT change, so F cannot do any work!.

Now, let us reduce the problem to the known sign given above. A basic technique is: since we know $\partial(S,T)/\partial(L,T)$, we should throw factors $\partial(S,T)$ and $\partial(L,T)$ into the formula and watch whether you can get sign-definite ratios (e.g., the diagonal terms such as $\partial S/\partial T$) or the factor that can be replaced with ± 1 with the aid of the Maxwell relations.

$$\frac{\partial S}{\partial F}\Big|_{L} = \frac{\partial (S,L)}{\partial (F,L)} = \frac{\partial (S,T)}{\partial (F,L)} \frac{\partial (S,L)}{\partial (S,T)} = \frac{\partial (S,L)}{\partial (S,T)} = \frac{\partial (S,L)}{\partial (T,L)} \frac{\partial (T,L)}{\partial (S,T)} = -\frac{C_{L}}{T} \frac{\partial (L,T)}{\partial (S,T)} = -\frac{C_{L}}{T} \left| \frac{\partial S}{\partial L} \right|_{T} > 0$$

Notice that we have used a Maxwell's relation (in the form given in 4; notice that the usual Maxwell's rule is hard to apply in this case; try). If you throw in $\partial(T, L)$ first, instead of $\partial(S, T)$, you still need a Maxwell, and the logic

and the difficulty (or ease) are about the same:

$$\begin{split} \frac{\partial S}{\partial F}\Big|_{L} &= \left. \frac{\partial (S,L)}{\partial (F,L)} = \frac{\partial (L,T)}{\partial (F,L)} \frac{\partial (S,L)}{\partial (L,T)} = \frac{C_{L}}{T} \frac{\partial (T,L)}{\partial (F,L)} \\ &= \left. \frac{C_{L}}{T} \frac{\partial (T,L)}{\partial (S,T)} \frac{\partial (S,T)}{\partial (F,L)} = \frac{C_{L}}{T} \frac{\partial (T,L)}{\partial (S,T)} = - \frac{C_{L}}{T} \left/ \left. \frac{\partial S}{\partial L} \right|_{T} > 0. \end{split}$$