**Important Corrections to Stowe by Dan Schroeder—Spring 2000**

## 1. Chemical Potential

In Section 6C, Stowe introduces a quantity called $\mu$, the chemical potential. One correct way to define it is

$$\mu \equiv \left.\frac{\partial E}{\partial N}\right|_{S,V},$$

i.e., the change in a system's internal energy as you add one particle while holding the entropy and volume fixed. If you think of the process of adding a particle to a system, it's clear that the system's energy might change for a variety of reasons. For instance, the whole system might be sitting on a mountain top, so to add a particle you might need to give it a lot of gravitational potential energy. Or in a solid, to add a particle you might need to create some chemical bonds, which store (negative) potential energy. Stowe explains this point quite well. The problem is that he also says in places that this type of potential energy is the *only* contribution to $\mu$ and that just isn't true. Even in an ideal gas (with no chemical bonds) at sea level (no gravitational energy), it turns out that $\mu$ is nonzero. The reason is that pesky subscript $S$ on the partial derivative. Normally when you add a particle to a system, the entropy is *not* fixed. If you want to keep $S$ fixed, you typically have to remove some energy from the system as you add the particle. So $\mu$ for an ideal gas is actually negative.

Most of the discussion in Section 6C is however correct if you use a different symbol, say $\mu_0$, wherever $\mu$ appears, and if you realize that $\mu_0$ is just one part of the chemical potential, not the whole thing. The first law as written in the grey box on page 93 is correct only if we adopt a rather restricted definition of heat and work, saying for instance that no work is involved when you lift a particle onto a mountain top. In point of fact it's rarely necessary to classify energy transfers as heat or work when particles are entering or leaving a system. Similarly, on page 138 the symbol $\mu$ should again be changed to $\mu_0$.

Chemical potential comes up next in Chapter 11. The equation on page 174 is perfectly correct (and is what Stowe really meant by the equation on page 93). However the discussion in Section A again suffers from the misconception that potential energy is the only contribution to $\mu$. The equations in Sections C through E are all fine. The discussion in Section F is again misleading and incomplete.

As far as I'm aware, all equations involving $\mu$ in the next several chapters are correct, until pages 374–375 where all of the equations are wrong. The rest of Chapter 22 seems to be fine however. The error recurs briefly on page 392. The last occurrence of this error is on page 445, where Stowe is correct in claiming that $\mu = 0$ for a photon gas but gives the wrong reason. Here are two correct

reasons, both based on the fact that photons can be created or destroyed in any quantity; their total number is not conserved.

First consider the Helmholtz free energy, which must attain the minimum possible value at equilibrium with $T$ and $V$ held fixed (cf. Sears & Salinger Section 7–1 for a derivation of this fact). In a system of photons, the number $N$ of particles is not constrained but rather takes whatever value will minimize $F$. If $N$ then changes infinitesimally, $F$ should be unchanged, so that

$$\mu = \left.\frac{\partial F}{\partial N}\right|_{T,V} = 0.$$

A second argument makes use of the condition for chemical equilibrium. Consider a typical reaction in which a photon $\gamma$ is created or absorbed by an electron,

$$e \leftrightarrow e + \gamma.$$
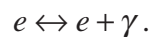
The equilibrium condition for such a reaction is given by Eq. (22.7),

$$(-1)\mu_e + (+1)\mu_e + (+1)\mu_\gamma = 0.$$

In other words, the chemical potential for photons is zero.

## 2. Multiplicity of a Classical System

On page 111, Stowe introduces a miraculous formula for the density of states, or equivalently, the multiplicity, of a system with $\mathcal{N}$ degrees of freedom,

$$g(E) \propto E^{\mathcal{N}/2}.$$

(This formula is derived in the appendix to Chapter 7.) What you need to know is that this formula is true only for *classical*, i.e., non-quantum, systems. It holds when molecules have so much internal energy that the discrete levels are not noticeable. (This occurs when the degrees of freedom are not frozen out.) The formula fails for most systems at low temperatures and sometimes room temperature is low in this sense. For exotic systems like a paramagnet, where the idea of degrees of freedom makes no sense at all, the formula fails completely.

## 3. Counting Polarization States

At the top of page 430, Stowe introduces an original formula for the number of polarization states $\lambda$ of a particle, in terms of its spin $j$. The first half of the formula, $\lambda = 2j + 1$ for massive particles, is fine. However, the second half, $\lambda = 2j$ for massless particles, is not a fundamental law and only accidentally works for photons and neutrinos. It is wrong, for instance, for gravitons which have $j = 2$ but only two polarization states.