Notes on Statistical Mechanics by Pathria

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Contents

Natural units will be used hahahaha $\hbar = c = k_B = 1$

1   Axioms and Derivation of Thermodynamic Quantities and Formule

- The axiom of statistial mechanics is called "equal *a priori* probabilities", that states:

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  When there are no additional constraints, a given macrostate of the system at any
  time is equally likely to be found in any one of its microstates.
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- The number of macrostates is written as a function of the extensive variables $\Omega(N, V, E)$ representing number of particles, volume and total energy respectively.

  > **Definition**: Equilibrium is when a system is at a macrostate with the maximum number of microstates. Which is equivilent to when Ω is maximized.

- Firstly we will derive temperature and entropy from our axiom and definition of equilibrium.

  > **Derivation**: Take two physical systems at equilibrium: A_1 at N_1, V_1, E_1 and A_2 at N_2, V_2, E_2. Now have them contact such that the the volume doesn't change but energy is allowed to be transfered from one system to another.
  > Energy is conserved, thus E^0 is constant,
  > $$E^0 \equiv E_1 + E_2 \tag{1}$$
  > When the two systems reach equilibrium again at equilibrium energies $\overline{E_1}$ and $\overline{E_2}$ respectively, by definition

the total number of macrostates $\Omega_1(E_1)\Omega_2(E_2)$ is maximized. Thus,

$$\frac{\partial}{\partial E_1}(\Omega_1(E_1)\Omega_2(E_2)) = 0 \tag{2}$$

Using the product rule and chain rule,

$$\left.\frac{\partial \Omega_1(E_1)}{\partial E_1}\right|_{E_1=\overline{E_1}} \Omega_2(E_2) + \Omega_1(E_1)\left.\frac{\partial \Omega_2(E_2)}{\partial E_2}\right|_{E_2=\overline{E_2}} \frac{\mathrm{d}E_2}{\mathrm{d}E_1} = 0 \tag{3}$$

Noting that $dE_2/dE_1 = -1$ from equation (1)

$$\left.\frac{\partial \Omega_1(E_1)}{\partial E_1}\right|_{E_1=\overline{E_1}} \Omega_2(E_2) = \Omega_1(E_1)\left.\frac{\partial \Omega_2(E_2)}{\partial E_2}\right|_{E_2=\overline{E_2}} \tag{4}$$

Taking advantage of the fact that the derivative of $\log u$ is u'/u

$$\left.\frac{\partial \log(\Omega_1(E_1))}{\partial E_1}\right|_{E_1=\overline{E_1}} = \left.\frac{\partial \log(\Omega_2(E_2))}{\partial E_2}\right|_{E_2=\overline{E_2}} \tag{5}$$

Notice that these it is only possible to be in equilibrium when these two quantities are equal. In general, define

$$\beta \equiv \left(\frac{\partial \log \Omega}{\partial E}\right)_{N,V,E=\overline{E}} \tag{6}$$

This resembles the behavior of the thermodynamic temperature and should be somewhat related. Furthermore, recall from the second law

$$\left(\frac{\partial S}{\partial E}\right)_{N,V} = \frac{1}{T} \tag{7}$$

And thus,

$$\frac{\Delta S}{\Delta \log \Omega} = \frac{1}{\beta T} = \text{constant} \tag{8}$$

This constant is known as Boltzmann's constant k, and thus

$$S = k \log \Omega \tag{9}$$

This is the definition of entropy. Zero entropy represents when there is only one microstate, which is consistent.

- Now the other intensive quantities pressure and chemical potential can be realized with a similar approach.

Derivation: Recall the basic formula of thermodynamics

$$\mathrm{d}E = T\mathrm{d}S - P\mathrm{d}V + \mu\mathrm{d}N \tag{10}$$

Now assume that the barrier between the two systems is movable. Then, the volumes are able to change with $V_1 + V_2$ constant. From the similar derivation above

$$\left.\frac{\partial \log \Omega_1}{\partial V_1}\right|_{V_1=\overline{V_1}} = \left.\frac{\partial \log \Omega_2}{\partial V_2}\right|_{V_2=\overline{V_2}} \tag{11}$$

In a similar fashion, define

$$\eta \equiv \left(\frac{\partial \log \Omega}{\partial V}\right)_{N,E,V=\overline{V}} \tag{12}$$

This quantity can be rewritten as

$$\eta = \frac{\partial \log \Omega}{\partial E}\frac{\mathrm{d}E}{\mathrm{d}V} = \frac{P}{kT} \tag{13}$$

as $\frac{\partial \log \Omega}{\partial E}$ is $\frac{1}{kT}$ from above and dE/dV is the thermodynamic pressure P from (10).
Similarly, if particles are allowed to be transfered from one system to the other then at equilibrium,

$$\left.\frac{\partial \log \Omega_1}{\partial N_1}\right|_{N_1=\overline{N_1}} = \left.\frac{\partial \log \Omega_2}{\partial N_2}\right|_{N_2=\overline{N_2}} \tag{14}$$

Define
$$\zeta \equiv \left(\frac{\partial \log \Omega}{\partial N} \right)_{V,E,N=\overline{N}} \tag{15}$$

Again using chain rule and (10),
$$\zeta = \frac{\partial \log \Omega}{\partial E} \frac{\mathrm{d}E}{\mathrm{d}N} = -\frac{\mu}{kT} \tag{16}$$

Note that at equilibrium, $T_1 = T_2$, $P_1 = P_2$, and $\mu_1 = \mu_2$ as expected.

- In S.I. Units, boltzmann's constant is $k \approx 1.38 \times 10^{-23} \mathrm{J/K}$. We will use natural units so $k = 1$.

- Using basic calculus and the following lemma, the rest of thermodynamics can be derived

  Lemma 1: If three variables are muturally related,
  $$\left(\frac{\partial x}{\partial y} \right)_z \left(\frac{\partial y}{\partial z} \right)_x \left(\frac{\partial z}{\partial x} \right)_y = -1 \tag{17}$$

  "The proof is left as an exercise to the reader"—James Davis

  The mathematics will not be shown here, but a few things should be noted
  - Following (10), the intrinsic fields can be written as
    $$P = -\left(\frac{\partial E}{\partial V} \right)_{N,S} \qquad \mu = \left(\frac{\partial E}{\partial N} \right)_{V,S} \qquad T = \left(\frac{\partial E}{\partial S} \right)_{N,V} \tag{18}$$

  - The Helmholtz free energy A, Gibbs free energy G and enthalpy H are given by
    $$A = E - TS \tag{19}$$
    $$G = A + PV = E - TS + PV = \mu N \tag{20}$$
    $$H = E + PV = G + TS \tag{21}$$

  - Since the specific heat is $C = \frac{\mathrm{d}Q}{\mathrm{d}T} = \frac{T\mathrm{d}S}{\mathrm{d}T}$, the specific heat at constant volume C_V and the specific heat at constant pressure C_P are
    $$C_V = T \left(\frac{\partial S}{\partial T} \right)_{N,V} = \left(\frac{\partial E}{\partial T} \right)_{N,V} \tag{22}$$

  and
    $$C_P = T \left(\frac{\partial S}{\partial T} \right)_{N,P} = \left(\frac{\partial (E + PV)}{\partial T} \right)_{N,P} = \left(\frac{\partial H}{\partial T} \right)_{N,P} \tag{23}$$

1.1 Ideal Gas Law

1.1.1 Simple Derivation

- The assumption for the ideal gas is that the probability of finding any of the particles in any region of the available volume is independent of the locations of all other particles. Then, the total number of ways in which N particles can be distributed is just equal to the product of the number of ways each particle is found in a given region, which is proportional to V. Thus,
  $$\Omega(N, E, V) \propto V^N \tag{24}$$

  Derivation: From (13), and assuming a proportionality constant c for (24)
  $$\frac{P}{T} = \left(\frac{\partial \log \Omega(N, E, V)}{\partial V} \right)_{N,E} = \frac{\mathrm{d}}{\mathrm{d}V}(N \log V + \log c) = \frac{N}{V} \tag{25}$$

  since $N = nN_A$ where N_A is Avagadro's number, (25) can be rearranged as $PV = nRT$ where $R = N_A$ ($k = 1$ is used). This holds for any classical system composed of noninteracting particles.

1.1.2 More General Quantum Mechanical Derivation

- Now model the system as a quantum-mechanical infinite well (3D) with side-lengths $L = V^{1/3}$. The bound state energies of the system (which can be derived by solving the time-independent Schrodinger equation) are

$$\epsilon(n_x, n_y, n_z) = \frac{\pi^2}{2mL^2}(n_x^2 + n_y^2 + n_x^2); \quad n_x, n_y, n_z \in \mathbb{Z}_+ \tag{26}$$

For a single (non-relativistic) particle at a given energy, the number of microstates is equal to the number of independent energy eigenstates with that energy, i.e.

$$(n_x^2 + n_y^2 + n_z^2) = \frac{2mV^{2/3}\epsilon}{\pi^2} = \epsilon^* \tag{27}$$

The number of solutions to (27) is also $\Omega(1, \epsilon, V)$ since it's 1 particle, ϵ energy, and V volume.

- This model can be extended further to suggest that $\Omega(N, E, V)$ may be equal to the number of independent solutions to

$$\sum_{r=1}^{3N} n_r^2 = \frac{2mV^{2/3}E}{\pi^2} = E^* \tag{28}$$

for N independent (non-interacting) particles in an infinite well. The number of solutions or $\Omega(N, E, V)$ can only depend on N and E^*. As E^* is a constant multiple of $V^{2/3}E$, the E and V dependence of $\Omega(N, E, V)$ is $V^{2/3}E$. Therefore,

$$S(N, V, E) \equiv k \log \Omega(N, V, E) \equiv k \log \Omega(N, V^{2/3}E) \equiv S(N, V^{2/3}E) \tag{29}$$

> **Derivation**: For a *reversible adiabatic process* where S and N are constant, $V^{2/3}E = c$ constant due to (29). From (18)
>
> $$P = -\left(\frac{\partial E}{\partial V}\right)_{N,S} = -\frac{\mathrm{d}}{\mathrm{d}V}cV^{-2/3} = \frac{2}{3}(cV^{-2/3})V^{-1} = \frac{2}{3}\frac{E}{V} \tag{30}$$
>
> The pressure of a system of non-relativistic, non-interacting particles is exactly $\frac{2}{3}$ of its energy density. Rearranging (30), $E = \frac{2}{3}PV$. Since $c = V^{2/3}E = V^{2/3}\frac{2}{3}PV \implies PV^{5/3} = \frac{3}{2}c$ constant.

- For a specific value of E^*, the problem of finding integer solutions to (28) can be reframed as finding integer lattice points on the surface of a $3N$ dimensional hypersphere with radius $\sqrt{E^*}$. This is very difficult to count. So first, consider a simper case of counting all lattice points inside the "positive part" of the volume of the hypersphere. This can be seen as the number of microstates with energy less than or equal to E (with the same V of course). This volume will be called $\Sigma(E^*)$

- These formulas are given by mathematicians and **should not** be questioned.

   1. The volume of a N dimensional hypersphere as a function of its radius is

$$V(N, R) = \frac{\pi^{n/2}}{(n/2)!}R^N \tag{31}$$

   2. The *Sterling Approximation* states that for big n

$$\log(n!) \approx n \log n - n \tag{32}$$

- Since the number of integer lattice points contained in a continuous region is approximately equal to the volume of the region itself, using (31), and resubstituting the definition of E^* from (28)

$$\Sigma(E^*) \approx \left(\frac{1}{2}\right)^{3N}\left(\frac{\pi^{3N/2}}{(3N/2)!}E^{*3N/2}\right) = \frac{V^N}{(3N/2)!}\left(\frac{mE}{2\pi}\right)^{3N/2} \tag{33}$$

Note that the $\left(\frac{1}{2}\right)^{3N}$ comes from the fact that only the positive part of the hypersphere is considered. Now taking logarithm using (32),

$$\log \Sigma(N, V, E) \approx N \log\left[V\left(\frac{mE}{2\pi}\right)^{3/2}\right] - \frac{3}{2}N \log\left(\frac{3}{2}N\right) + \frac{3}{2}N = N \log\left[V\left(\frac{mE}{3\pi N}\right)^{3/2}\right] + \frac{3}{2}N \tag{34}$$

- Since the simpler problem is solved, we can tackle the original problem. Now the enemy (you) imposed a small $\epsilon << E$ on the order $\epsilon/E = \mathcal{O}(1/\sqrt{N})$ where the number of microstates $\Omega(N, V, E)$ with total energy between $E - \frac{1}{2}\epsilon$ and $E + \frac{1}{2}\epsilon$ is to be found. Using local linear approximation,

$$\Omega(N, V, E) \approx \frac{\partial \Sigma(N, V, E)}{\partial E}\bigg|_E \epsilon = \frac{3N}{2}\frac{V^N}{(3N/2)!}\left(\frac{m}{2\pi}\right)^{3N/2}E^{3N/2-1}\epsilon = \frac{3N\epsilon}{2E}\Sigma(N, V, E) \tag{35}$$

Taking the logarithm and substituting (34),

$$\log \Omega(N, V, E) \approx \log \Sigma(N, V, E) + \log\left(\frac{3}{2}N\right) + \log\left(\frac{\epsilon}{E}\right) \tag{36}$$

- The leading term $\log \Sigma(N, V, E)$ is $\mathcal{O}(N)$. The second term is trivially $\mathcal{O}(\log N)$. The final term is slightly more complicated. Since ϵ/E is $\mathcal{O}(N^{-1/2})$, its logarithm is likely negative. But more importantly, its magnitude is $\mathcal{O}(\log N)$. As N becomes very large, only the leading term has a significant contribution; thus,

$$\log \Omega \approx \log \Sigma \approx N \log\left[V\left(\frac{mE}{3\pi N}\right)^{3/2}\right] + \frac{3}{2}N \tag{37}$$

- Note two things. Firstly, the ϵ imposed by the enemy is insignificant. As long as it is similar to $\mathcal{O}(N^{-1/2})$, its contribution is insignificant relative to the other terms. Secondly, as $\log \Omega \approx \log \Sigma$ shows that the rate at which the number of microstates of the system increases as a function of energy is so great, that the microstates with energies 0 to $E - \frac{1}{2}\epsilon$ are very few and far between compared to those with energies near E.

- With a good approximation for $\log \Omega$, the rest of the thermodynamics can be derived.

  Derivation: First of all, from the definition of entropy (9),

  $$S(N, V, E) = \log \Omega = N \log\left[V\left(\frac{mE}{3\pi N}\right)^{3/2}\right] + \frac{3}{2}N \tag{38}$$

  Isolating the energy E,

  $$E(S, N, V) = \frac{3\pi N}{mV^{2/3}} \exp\left(\frac{2S}{3N} - 1\right) \tag{39}$$

  From (18),

  $$\left(\frac{\partial S}{\partial E}\right)_{N,V} = \frac{1}{T} = \frac{3}{2}\frac{N}{E} \tag{40}$$

  $$E = \frac{3}{2}NT = \frac{3}{2}nRT \tag{41}$$

  Using (22), the specific heat at constant volume is

  $$C_V = \left(\frac{\partial E}{\partial T}\right)_{N,V} = \frac{3}{2}nR \tag{42}$$

  From (30),

  $$P = \frac{2}{3}\frac{E}{V} = \frac{nRT}{V} \implies PV = nRT \tag{43}$$

  From (23), the specific heat at constant pressure is

  $$C_P = \left(\frac{\partial H}{\partial T}\right)_{N,V} = C_V + \frac{\mathrm{d}}{\mathrm{d}T}(PV) = \frac{3}{2}nR + nR = \frac{5}{2}nR \tag{44}$$

  Then the ratio between the two specific heats is

  $$\gamma \equiv \frac{C_P}{C_V} = \frac{5}{3} \tag{45}$$

- Suppose the ideal gas undergoes an *isothermal change* with constant T and N. From (41), the energy E remains constant. Using logarithm laws, the entropy can be rewritten as

$$S(N, V, E) = N \log V + N \log\left[\left(\frac{mE}{3\pi N}\right)^{3/2}\right] + \frac{3}{2}N \tag{46}$$

Since T, N, E, m are all constants, the only term that changes is the leading term. Thus,

$$\Delta S = N \log\left(\frac{V_f}{V_i}\right) \tag{47}$$

2 Gibb's Paradox and Correction

2.1 Entropy of Mixing

- Mixing two ideal gasses at the same temperature each with entropy

$$S_i = N_i \log V_i + \frac{3}{2} N_i \left[1 + \log \left(\frac{m_i T}{2\pi} \right) \right] \qquad i = 1, 2 \tag{48}$$

After the mixing, the change in entropy (known as the *entropy of mixing*) would be

$$\Delta S = \sum_{i=1}^{2} N_i \log(V_1 + V_2) + \frac{3}{2} N_i \left[1 + \log \left(\frac{m_i T}{2\pi} \right) \right] - \sum_{i=1}^{2} N_i \log V_i + \frac{3}{2} N_i \left[1 + \log \left(\frac{m_i T}{2\pi} \right) \right]$$
$$= N_1 \log \left(\frac{V_1 + V_2}{V_1} \right) + N_2 \log \left(\frac{V_1 + V_2}{V_2} \right) \tag{49}$$

- For the case where the number densities of the two ideal gases are different, mixing should be an irreversible process. This is indeed true as $\Delta S > 0$.

- If the number densities of the two ideal gases are equal, mixing should be reversible as the partition can be reinserted and nothing should have change. Thus, it is expected that $\Delta S = 0$. However, if $V = \alpha N$,

$$\Delta S = N_1 \log \left(\frac{N_1 + N_2}{N_1} \right) + N_2 \log \left(\frac{N_1 + N_2}{N_2} \right) > 0 \tag{50}$$

This suggests that there must be an omission that has occured.

- Approximating $\log(n!) \approx n \log n - n \approx n log n$ for big n, (50) can be simplified to

$$\Delta S = S_f - S_1 - S_2 \approx \log[(N_1 + N_2)!] - \log(N_1!) - \log(N_2!) \tag{51}$$

From the simplified expression, it seems like executing $S -= \log(N!)$; would resolve this issue (challenge, sorry praxis). This is the solution recommended by Gibbs.

- With this modification,

$$S(N, V, E) = N \log \left[\frac{V}{N} \left(\frac{mE}{3\pi N} \right)^{3/2} \right] + \frac{5}{2} N \tag{52}$$

$$= N \log \left(\frac{V}{N} \right) + \frac{3}{2} N \left[\frac{5}{3} + \log \left(\frac{mT}{2\pi} \right) \right] \tag{53}$$

- This also resolves another issue. The entropy of the ideal gas derived in (38) does not behave like an extensive property of the system. If all intensive variables are held constant and the size of the system is doubled, the entropy should also double.

$$S(2N, 2V, 2E) - 2S(N, V, E) = \left[(2N) \log \left[(2V) \left(\frac{m(2E)}{3\pi(2N)} \right)^{3/2} \right] + \frac{3}{2}(2N) \right] - \left[2N \log \left[V \left(\frac{mE}{3\pi N} \right)^{3/2} \right] + 3N \right]$$
$$= 2N \log 2 \tag{54}$$

With the modification, entropy described by (52) does behave like an extensive field!

$$S(\alpha N, \alpha V, \alpha E) = \alpha S(N, V, E) \tag{55}$$

- The corrected entropy of mixing would be

$$\Delta S = (N_1 + N_2) \log \left(\frac{V_1 + V_2}{N_1 + N_2} \right) - N_1 \log \left(\frac{V_1}{N_1} \right) - N_2 \log \left(\frac{V_2}{N_2} \right) \tag{56}$$

Here when $N_1/V_1 = N_2/V_2$, ΔS is indeed zero!

2.2 More on the Ideal Gas

- The quantities related to the chemical potential can now be derived as the correction is nessecary to derive the correct result.

> **Derivation:** With the correction, the energy must be rederived. Firstly, isolating for the energy,
>
> $$E(S, N, V) = \frac{3\pi N^{5/3}}{mV^{2/3}} \exp\left(\frac{2S}{3N} - \frac{5}{2}\right) \tag{57}$$
>
> The chemical potential can also be derived
>
> $$\mu = \left(\frac{\partial E}{\partial N}\right)_{V,S} = E\left(\frac{5}{3N} - \frac{2S}{3N^2}\right) \tag{58}$$
>
> From equations (30) and (41),
>
> $$\mu = \frac{1}{N}\left(E + \frac{2}{3}E - \frac{2S}{3N}\right) = \frac{1}{N}(E + PV - TS) \equiv \frac{G}{N} \tag{59}$$
>
> In terms of the variables N, V, T, the chemical potential is expressed as
>
> $$\mu(N, V, T) = T \log\left[\frac{N}{V}\left(\frac{2\pi}{mT}\right)^{3/2}\right] \tag{60}$$
>
> The Helmholtz free neergy is
>
> $$A = E - TS = G - PV = N(\mu - T) = NT\left[\log\left[\frac{N}{V}\left(\frac{2\pi}{mT}\right)^{3/2}\right] - 1\right] \tag{61}$$

- Note that the Helmholtz free energy is an extensive property whereas the chemical potential is an intensive property.

2.3 Indistinguishable Particles

- The reason that the original derivation of the entropy of the system of N non-interacting particles requires the correction is because the derivation assumes that the particles are distinguishable.

- In reality, the most particles are identical. This means that for 2 particles, the state with $|1\rangle \otimes |2\rangle$ and $|2\rangle \otimes |1\rangle$ are indistinguishable and only considered as 1 microstate. Therefore, the original derivation overcounted the number of microstates (by $N!$).

- The correct way to represent a system is to represent its particles distribution over energies by numbers.

$$E = \sum_{i=0}^{\infty} n_i \epsilon_i \tag{62}$$

where $n_0, n_1, n_2 \dots$ represent the number of particles in the system with energy $\epsilon_0, \epsilon_1, \epsilon_2 \dots$ respectively.

- The total number of microstates for a system of indistinguishable particles is then

$$\Omega = \frac{N!}{\prod n_i!} \tag{63}$$

3 Chapter 1 Problems

> **Solution 1 (1):**
>
> **(a)** Take the taylor expansion of $\log \Omega^0(E^0, E_1) = \log \Omega_1(E_1) + \log \Omega_2(E_2)$ at equilibrium energy $E_1 = \overline{E_1}$.
>
> $$\log \Omega^0(E_1) = \log \Omega_1(\overline{E_1}) + \log \Omega_2(\overline{E_2}) + \left(\left.\frac{\partial \log \Omega_1}{\partial E_1}\right|_{E_1=\overline{E_1}} + \left.\frac{\partial \log \Omega_2}{\partial E_2}\right|_{E_2=\overline{E_2}} \frac{dE_2}{dE_1}\right)(E_1 - \overline{E_1})$$
>
> $$+ \frac{1}{2}\left(\left.\frac{\partial^2 \log \Omega_1}{\partial E_1^2}\right|_{E_1=\overline{E_1}} + \left.\frac{\partial^2 \log \Omega_2}{\partial E_2^2}\right|_{E_2=\overline{E_2}}\left(\frac{dE_2}{dE_1}\right)^2 + \left.\frac{\partial \log \Omega_2}{\partial E_2}\right|_{E_2=\overline{E_2}} \frac{d^2 E_2}{dE_1^2}\right)(E_1 - \overline{E_1})^2 \tag{64}$$
>
> $$+ \mathcal{O}\left[(E_1 - \overline{E_1})^3\right]$$

The linear term of the series is zero as the taylor expansion is taken at equilibrium energies (see (3) and (5)). In the quadratic term, the third contribution is also zero as the 2nd derivative of E_2 is zero. For the remaining part of the quadratic term,

$$\left.\frac{\partial^2 \log \Omega}{\partial E^2}\right|_{E=\overline{E}} = \frac{\partial}{\partial E}\frac{1}{T} = \frac{\partial T}{\partial E}\frac{\partial}{\partial T}\frac{1}{T} = -\frac{1}{C_V T^2} \tag{65}$$

Define

$$\frac{1}{a^2} \equiv \frac{1}{C_{V1}T^2} + \frac{1}{C_{V2}T^2} \tag{66}$$

Simplifying,

$$\log \Omega^0(E_1) = \log \Omega^0(\overline{E_1}) - \frac{(E_1 - \overline{E_1})^2}{2a^2} + \mathcal{O}\left[(E_1 - \overline{E_1})^3\right] \tag{67}$$

The $\mathcal{O}\left[(E_1 - \overline{E_1})^3\right]$ term can be neglected since when the systems become large, the temperature becomes less dependent on the energy. Exponentiating both sides of (67),

$$\Omega^0(E_1) = \Omega^0(\overline{E_1})\exp\left(-\frac{(E_1 - \overline{E_1})^2}{2a^2}\right) \tag{68}$$

Thus, the root-mean-square deviation of E_1 is a in (66).

(b) For the ideal gas, $C_V = \frac{3}{2}N$ from (42). Thus,

$$\frac{1}{a^2} = \frac{1}{N_1 T^2} + \frac{1}{N_2 T^2} \tag{69}$$

$$a = T\sqrt{\frac{N_1 + N_2}{N_1 N_2}} \tag{70}$$

Where T is the equilibrium temperature.

Solution 2 (1): The total entropy S and number of microstates and Ω are that for n systems with entropies $S_1, S_2 \ldots S_n$ and number of microstates $\Omega_1, \Omega_2 \ldots \Omega_n$,

$$S = \sum_{j=1}^{n} S_i \qquad \Omega = \prod_{j=1}^{n} \Omega_i \tag{71}$$

$$S = f(\Omega) = \sum_{j=1}^{n} f(\Omega_i) \tag{72}$$

Combining the definitions,

$$f\left(\prod_{j=1}^{n} \Omega_i\right) = \sum_{j=1}^{n} f(\Omega_i) \tag{73}$$

It is shown by Dieudonné, Jean in *Foundations of Modern Analysis* (1969) pp. 84 that the only functions satisfying this definition are logarithmic functions.

Solution 3 (1): The total