

**Problem Set PS08**  
ISSUED: 10/25/01 **Due: 11/1/01**

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Name \_\_\_\_\_

**Instructions.** Complete all questions before class on the due date. You are encouraged to work together. Be sure to struggle with the problem before seeking help. Many of the exercises are very similar to problems in the book. Understanding the solution to these problems will be helpful in completing the assigned exercises.

**Mathematical Exercises**

1. The trace of a matrix  $M$  (written  $\text{Tr}[M]$ ) is simply the sum of the diagonal elements of  $M$ . By diagonal one means top left to bottom right. Evaluate the trace for the following matrices.

(a)

$$M = \begin{bmatrix} 1 & 5 & -6 \\ -1 & 2 & 4 \\ 7 & 9 & -1 \end{bmatrix}$$

(b)

$$M = \begin{bmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \lambda_3 \end{bmatrix}$$

2. Associated with matrices are eigenvectors and eigenvalues. These are analogues of the eigenfunctions and eigenvalues we have worked with for operators. That is, the column vector  $V$  is an eigenvector of the matrix  $M$  corresponding to the eigenvalue  $\lambda$  if

$$MV = \lambda V.$$

We will not learn how to calculate eigenvectors and eigenvalues in this course (if you had linear algebra you did quite a lot of this), but MATHEMATICA can quickly calculate eigenvectors and eigenvalues. Use MATHEMATICA to determine the eigenvectors and eigenvalues of the following matrices. Comment on your answer for (b) also compare the sum of the eigenvalues for parts (a) and (b) to the answers you got for the traces in the preceding problem.

(a)

$$M = \begin{bmatrix} 1 & 5 & -6 \\ -1 & 2 & 4 \\ 7 & 9 & -1 \end{bmatrix}$$

(b)

$$M = \begin{bmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \lambda_3 \end{bmatrix}$$

3. The geometric series is defined as

$$\sum_{n=0}^{\infty} x^n = 1 + x + x^2 + x^3 + \dots$$

This series can, in fact, be written in *closed form* as

$$\sum_{n=0}^{\infty} x^n = \frac{1}{1-x}.$$

(a) For what values of  $x$  is this series valid?

(b) Write

$$1 + f(r) + f(r)^2 + f(r)^3 + \dots,$$

where  $f(r)$  is some arbitrary function of  $r$ , in closed form and in series notation (i.e.,  $\sum$  notation).

(c) Write

$$1 + \sin x + (\sin x)^2 + (\sin x)^3 + \dots$$

in closed form and in series notation. Use MATHEMATICA to plot the closed form expression and the first 500 terms in the series. At what point does the truncated series deviate from the closed form expression? why?

(d) Write

$$1 + e^{-\beta x} + e^{-2\beta x} + e^{-3\beta x} + \dots$$

in closed form and in series notation.

## Exercises

4. A vial containing  $10^{20}$  bromine molecules is at 300K. How many molecules are in each of the first four vibrational states assume the harmonic oscillator model applies. (The stretching mode of bromine is  $325\text{cm}^{-1}$ ). Note we will often need to know the so-called thermal energy ( $kT$ ) in units of wavenumbers. You may want to download my  $kT$  calculator from the “files to download” section of the PChem website.
5. Derive the closed form canonical partition function for an ensemble of harmonic oscillators,

$$q_{HO} = \frac{e^{-\frac{1}{2}\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}},$$

from the series representation. Also show  $q_{HO} = \frac{1}{2 \sinh \frac{1}{2}\beta\hbar\omega}$ . Note: Eq. (4.32) in the notes should have a factor of 2 in the denominator. Finally separately plot  $q_{HO}$  as a function of temperature and then as a function of frequency. What do each of these plots mean physically? (It might be helpful to check out Castro’s legacy project from three years ago)

6. Later on we will derive a relation between pressure,  $P$ , and the partition function to be

$$P = \frac{1}{\beta} \left( \frac{\partial \ln Q}{\partial V} \right)_{n,\beta}.$$

For an ideal monatomic gas we have to worry only about translation of the gas in its container (volume  $V$ ). Thus the partition function is (ignoring the  $1/N!$  factor)

$$Q = q_{\text{mol}}^N = q_{\text{trans}}^N.$$

Using the translational partition function given on p72 of the notes, derive the ideal gas law. Note: the gas constant  $R = N_A k$  where  $N_A$  is Avogadro's number. Also the number of moles is  $n = N/N_A$ .

7. Consider the  $j^{\text{th}}$  particle of an ideal gas in a 3D cubic box (length  $a$  for each dimension) of volume  $V = a^3$ . Next semester we will solve the Schrödinger equation for this problem and find that the energy which now is described by three quantum numbers is

$$E_{n_x, n_y, n_z}^{(j)} = \frac{h^2}{8ma^2} (n_x^2 + n_y^2 + n_z^2).$$

The contribution that the  $j^{\text{th}}$  particle makes to the total pressure is given by

$$P^{(j)} = - \frac{dE_{n_x, n_y, n_z}^{(j)}}{dV}.$$

That is to say, the pressure is given by the amount of energy it takes to change the volume. **Use the equation  $V = a^3$  and the chain rule to show**

$$P^{(j)} = \frac{2E_{n_x, n_y, n_z}^{(j)}}{3V}.$$

Expressing this equation as an average one has

$$\bar{P} = \frac{2\bar{E}}{3V}.$$

We will learn in thermodynamics that  $\bar{E} = \frac{3}{2}NkT$  for an ideal gas of  $N$  particles. **Use this to obtain the ideal gas law** (note  $Nk = nR$ , **verify this**).

8. You probably have heard about Brownian motion—the random motion of small (but not microscopic) particles such as dust particles or mold spores in a fluid due to the incessant bombardment of molecules. Brownian motion was first reported and given attention by Brown, a botanist. Later Einstein and Smoluchoski independently put Brownian motion on a mathematical foundation. One nice mathematical description of Brownian motion is captured in the *Langevin equation* for the particles velocity  $v(t)$ :

$$\frac{dv(t)}{dt} = -\gamma v(t) + A(t)$$

The Langevin equations says that the change in velocity with time ( $\frac{dv(t)}{dt}$ ) is due to a frictional force ( $-\gamma v(t)$ ) which is proportional to the velocity itself and tends to slow the

motion plus a random force ( $A(t)$ ) which is due to the bombardment of the molecules on the particle. The Langevin equation is in the class of differential equations called *stochastic differential equations*. (Stochastic is a fancy word for random that makes you sound smart when you say it.) Formally one can handle stochastic differential equations in the same manner as regular differential equations, but one needs to consider averages when getting to the final solution. The formal solution to the Langevin equation is

$$v(t) = e^{-\gamma t} \int_0^t e^{\gamma t_1} A(t_1) dt_1 + v_0 e^{-\gamma t},$$

where  $v_0$  is the initial velocity. Let's consider the case where we simply place the particle in the fluid with zero initial velocity. Then

$$v(t) = e^{-\gamma t} \int_0^t e^{\gamma t_1} A(t_1) dt_1$$

Since  $A(t)$  is a random function, we can not evaluate the integral as is; we must consider averages. The average velocity is

$$\overline{v(t)} = \overline{e^{-\gamma t} \int_0^t e^{\gamma t_1} A(t_1) dt_1} = e^{-\gamma t} \int_0^t e^{\gamma t_1} \overline{A(t_1)} dt_1.$$

**Why can we go from the middle expression to the final expression?** Now we must think about the physical source of  $A(t)$ . It is due to bombardment of molecules against the particle. On average one would expect that there is equal bombardment from all directions. So therefore  $\overline{A(t)} = 0$ . **Does this make sense? What is  $\overline{v(t)}$ ?** One is also interested in the average of the square of the velocity  $\overline{v(t)^2}$ . This is slightly more complicated, but we begin with

$$\overline{v(t)^2} = \overline{e^{-\gamma t} \int_0^t e^{\gamma t_1} A(t_1) dt_1 \times e^{-\gamma t} \int_0^t e^{\gamma t_2} A(t_2) dt_2}.$$

**Rearrange this to the form**

$$\overline{v(t)^2} = e^{-2\gamma t} \int_0^t \int_0^t e^{\gamma t_1} e^{\gamma t_2} \overline{A(t_1)A(t_2)} dt_1 dt_2.$$

The  $\overline{A(t_1)A(t_2)}$  is called a *correlation function*. Correlation functions are extremely important in physical chemistry. This correlation function tells us how the value of  $A(t)$  at one point in time is related to the value of  $A(t)$  at another point in time. Again we must think about the physics to get a form for this correlation function. The particle experiences on collision with a molecule about every 10fs or so. Thus on the time scale of a person viewing the particle we can say that  $A(t)$  is completely random and therefore the values of  $A(t)$  at two distinct time points are completely unrelated (or uncorrelated). This translates mathematically to the fact that  $\overline{A(t_1)A(t_2)}$  is not zero only when  $t_1 = t_2$ . This means that the two integrals in the last equation are reduced to a single integral,

$$\overline{v(t)^2} = e^{-2\gamma t} \int_0^t e^{2\gamma t_1} dt_1.$$

**Evaluate this integral then plot and explain your result in terms of the physics of the problem.**

9. Consider a very intense laser excitation of matter such that the light–matter interaction is nonlinear:  $\mu(t) = \alpha(t)E(t)^3$ . Derive a nonlinear scattering equation analogous to Eq. (5.4) of the notes. Use trig identities to simplify the expression such that all the scattering frequencies are easily identified. These scattered frequencies are called third order processes. A number of processes occur at third order. These include (i) third harmonic generation, (ii) degenerate four wave mixing, (iii) coherent Stokes Raman scattering (CSRS pronounced scissors), (iv) coherent anti-Stokes Raman scattering (CARS) and some unnamed processes. Use your intuition to assign each of your derived frequencies to one of these processes.
10. I have mentioned in class that statistical mechanics preceded quantum mechanics. You might wonder how that can be since the energy levels from quantum mechanics appear explicitly in the Boltzmann distribution and in the canonical partition function. In fact one can define a classical Boltzmann distribution which describes the probability of finding a particle at position  $x$  with momentum  $p$  as

$$\frac{e^{-\beta H_{cl}(x,p)}}{Q} = \frac{e^{-\beta T_{cl}(p)} e^{-\beta V_{cl}(x)}}{Q}.$$

Let us apply in determining the pressure of the atmosphere at a function of altitude. Let  $x$  be the height above the earth’s surface. If we consider an infinitely tall cylinder of arbitrary area  $A$  that extends upwards from the surface of the earth. This cylinder contains  $N$  particles which are distributed according to the Boltzmann distribution

$$N(x, p) = N \frac{e^{-\beta T_{cl}} e^{-\beta V_{cl}}}{Q}.$$

Now focus on the potential energy term which we know from physics to be  $V_{cl}(x) = mgx$ . Using this we have

$$N(x, p) = N \frac{e^{-\beta T_{cl}}}{Q} e^{-\beta mgx}.$$

We could carefully evaluate  $N \frac{e^{-\beta T_{cl}}}{Q}$  but instead we will take the easy way out and say that this must be equal to the number of particles at sea level ( $x = 0$ ) which is just some constant  $N_0$ . Thus we have

$$N(x, p) = N(x) = N_0 e^{-\beta mgx}.$$

Use the ideal gas law (in the form  $P = \frac{NkT}{V}$ ) to derive the so-called barometric formula

$$P(x) = P_0 e^{\beta mgx}.$$

What would the total pressure and the partial pressure of oxygen be in an airplane that depressurized at 10km (Assume  $T = 298K$ )?

## Conceptual Problems

11. The thermal de Broglie wavelength is a measure of the “quantumness” of the ensemble. That is how much quantum character is manifest in the macroscopic system. Plot

the thermal de Broglie wavelength as a function of temperature. What does this say about the quantumness of the ensemble as a function of temperature? Superfluidity and superconductivity are very quantum in character. Based on your above argument, would you expect (macroscopic) superfluidity or superconductivity at high or low temperatures?

12. Using the classical theory of light scattering (Eq. (5.4) in the notes), sketch the Rayleigh, Stokes and anti-Stokes spectral lines for bromine. Assume bromine has one active mode ( $325\text{cm}^{-1}$ ) and assume the laser light used to do the scattering is at  $20000\text{cm}^{-1}$  (this is  $500\text{nm}$ —green light).

### Computer Problems

13. Consider a linear chain of  $N$  atoms. Each of the atoms can be in one of four states  $A$ ,  $B$ ,  $C$  or  $D$ , except that an atom in state  $A$  can not be adjacent to an atom in state  $B$  and an atom in state  $B$  can not be adjacent to an atom in state  $C$ . Find the entropy per atom for this system as  $N \rightarrow \infty$ . To solve this problem it is useful to define the set of four dimensional column vectors  $V^{(j)}$  such that the four elements are the total number of allowed configurations of a  $j$ -atom chain having the  $j^{\text{th}}$  atom in state  $A$ ,  $B$ ,  $C$ , or  $D$ . For example,

$$V^{(1)} = \begin{bmatrix} 1 \\ 1 \\ 1 \\ 1 \end{bmatrix}, \quad V^{(2)} = \begin{bmatrix} 3 \\ 2 \\ 3 \\ 4 \end{bmatrix}, \quad V^{(3)} = \begin{bmatrix} 10 \\ 6 \\ 10 \\ 12 \end{bmatrix}, \dots$$

The  $V^{(j+1)}$  can be found from the  $V^{(j)}$  vector using the matrix equation,

$$V^{(j+1)} = MV^{(j)},$$

where *for this example*

$$M = \begin{bmatrix} 1 & 0 & 1 & 1 \\ 0 & 1 & 0 & 1 \\ 1 & 0 & 1 & 1 \\ 1 & 1 & 1 & 1 \end{bmatrix}.$$

The matrix  $M$  is the so-called *transfer matrix* for this system. It can be shown that the number of configurations  $W = \text{Tr}[M^N]$ . Now for large  $N$ ,  $\text{Tr}[M^N] \approx \lambda_{\text{max}}^N$ , where  $\lambda_{\text{max}}$  is the largest eigenvalue of  $M$ . So

$$W = \lim_{N \rightarrow \infty} \lambda_{\text{max}}^N.$$

- Use  $M$  to find  $V^{(4)}$  and  $V^{(5)}$
- Verify  $V^{(2)}$  explicitly by drawing all the allowed 2-atom configurations.
- Verify  $W = \text{Tr}[M^N]$  for  $N = 1$  and  $N = 2$ .
- Use Boltzmann's equation to find the entropy per atom for this chain as  $N$  goes to infinity.

- (e) What is the entropy per atom for the case of  $N = 4$ . How does this compare to the large  $N$  answer.
14. Consider again the case of a linear chain having four possible monomer units  $A$ ,  $B$ ,  $C$  and  $D$ , but now the chain is formed such that  $A$  must always precede  $B$ ,  $C$  and  $D$ ;  $B$  must always precede  $C$  and  $D$ ; and  $C$  must always precede  $D$ . The transfer matrix for this case is

$$M = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 1 & 1 & 0 & 0 \\ 1 & 1 & 1 & 0 \\ 1 & 1 & 1 & 1 \end{bmatrix}$$

- (a) Use  $M$  to find  $V^{(2)}$ ,  $V^{(3)}$ ,  $V^{(4)}$  and  $V^{(5)}$
- (b) Verify  $V^{(3)}$  by writing out all allowed three atom chains
- (c) Use Boltzmann's equation to find the entropy per atom for this chain as  $N$  goes to infinity.

### Reflective Exercises

15. Considering your future career, think of a task you may be called upon to do that will make the PChem oral exams seem trivial (e.g., Ph.D. defense or having to inform a mother that her child has leukemia, etc.). Do you feel that you have the strength to complete the task in a professional manner?

① (a)  $T_r[M] = 1 + 2 - 1 = 2$

(b)  $T_r[M] = \lambda_1 + \lambda_2 + \lambda_3$

② eigenvalues  
6.31, -2.16 + 5.71i, -2.16 - 5.71i

eigenvectors:  $\begin{bmatrix} 0.90 + 1.21i \\ -0.45 - 0.31i \\ 1 \end{bmatrix}, \begin{bmatrix} 0.90 - 1.21i \\ -0.45 + 0.31i \\ 1 \end{bmatrix}, \begin{bmatrix} -0.21 \\ 0.98 \\ 1 \end{bmatrix}$

eigenvalues  $\lambda_1, \lambda_2, \lambda_3$  eigenvectors  $\begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix}, \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix}, \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix}$

③ (a) The series is valid for  $x \leq 1$

(b)  $1 + f(x) + f(x)^2 + f(x)^3 + \dots = \sum_{n=0}^{\infty} f(x)^n = \frac{1}{1-f(x)}$   
for  $f(x) \leq 1$

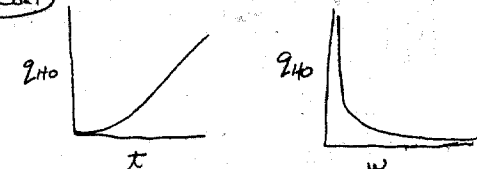
(c)  $1 + \sin x + \sin^2 x + \sin^3 x + \dots = \sum_{n=0}^{\infty} (\sin x)^n = \frac{1}{1-\sin x}$

Trouble with the series at  $x = \frac{\pi}{2}$   
here  $\sin \frac{\pi}{2} = 1$  near this point the higher order terms in the sum are important.

(d)  $1 + e^{-2x} + e^{-4x} + e^{-6x} + \dots = \sum_{n=0}^{\infty} (e^{-2x})^n = \frac{1}{1-e^{-2x}}$

④  $g_{Ho} = \frac{1}{2 \sinh \frac{\beta \hbar \omega}{2}} = \frac{1}{2 \sinh \frac{\beta \hbar \omega}{2}}$   
 $N_0 = 10^{20} \frac{e^{-\frac{\beta \hbar \omega}{2}}}{g_{Ho}} \quad N_1 = 10^{20} \frac{e^{-\frac{3\beta \hbar \omega}{2}}}{2g_{Ho}}$   
 $N_2 = \dots \quad N_3 = \dots$

⑤  $g_{Ho} = \sum_{n=0}^{\infty} e^{-\beta \hbar \omega (n + \frac{1}{2})} = e^{-\frac{\beta \hbar \omega}{2}} \sum_{n=0}^{\infty} e^{-\beta \hbar \omega n} = e^{-\frac{\beta \hbar \omega}{2}} \frac{1}{1 - e^{-\beta \hbar \omega}}$   
 $= \frac{1}{e^{\frac{\beta \hbar \omega}{2}} - 1} = \frac{1}{2 \sinh \frac{\beta \hbar \omega}{2}}$  ✓



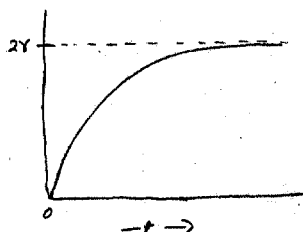
⑥  $E_n = \frac{V}{\Delta^2} \quad Q = \left(\frac{V}{\Delta^2}\right)^N$   
 $P = \frac{1}{\beta} \frac{\partial \ln Q}{\partial V} \quad \ln Q = \ln \left(\frac{V}{\Delta^2}\right)^N = N \ln V - N \ln \Delta^2$   
 $P = \frac{1}{\beta} \frac{\partial}{\partial V} (N \ln V - N \ln \Delta^2) = \frac{N}{\beta V} = \frac{NkT}{V}$   
 $P = \frac{NkT}{V}$  The ideal gas law

⑦  $p^{(i)} = - \frac{d \langle \ln \Omega \rangle}{dV} = - \frac{d \langle E \rangle}{dV}$   
 $\frac{d \langle E \rangle}{dV} = \frac{d \left( \frac{2 \hbar^2}{8ma^2} (n_x^2 + n_y^2 + n_z^2) \right)}{dV} = \frac{2 \hbar^2}{8ma^2} (n_x^2 + n_y^2 + n_z^2)$   
 $\frac{d \langle E \rangle}{dV} = \frac{1}{3a^2} = \frac{1}{3a^2}$   
so  $p^{(i)} = - \left( - \frac{2 \hbar^2}{8ma^2} \right) \left( \frac{1}{3a^2} \right) = \frac{2 \hbar^2}{12ma^4}$  ✓  
 $\bar{P} = \frac{2}{3} \frac{\bar{E}}{V} \quad \bar{E} = \frac{3}{2} NkT$   
 $\bar{P} = \frac{2}{3} \frac{3}{2} \frac{NkT}{V} \Rightarrow \bar{P} = \frac{NkT}{V}$  ideal gas law

⑧ We can go to from the middle expression to the final expression because only the  $A(x)$  is random and the integral of the average of  $A$  is the average of the integral of  $A$   
 $\bar{A} = 0$  makes sense because a collision that increases the velocity in one direction is matched by a collision in the opposite direction on average.

$$e^{-\gamma t} \int_0^t e^{\gamma t'} A(t') dt' \times e^{-\gamma t} \int_0^t e^{\gamma t''} A(t'') dt''$$
  
$$= \frac{e^{-\gamma t} e^{-\gamma t} \int_0^t \int_0^t e^{\gamma t'} e^{\gamma t''} A(t') A(t'') dt' dt''}{e^{-\gamma t} \int_0^t e^{\gamma t'} A(t') dt'}$$
  
$$= e^{-\gamma t} \int_0^t \int_0^t e^{\gamma(t'+t'')} A(t') A(t'') dt' dt''$$
 ✓

$\overline{V(x)^2} = e^{-2\gamma t} \int_0^t e^{2\gamma t'} dt'$   
 $= e^{-2\gamma t} \left[ \frac{1}{2\gamma} e^{2\gamma t'} \Big|_0^t \right]$   
 $= e^{-2\gamma t} \left[ \frac{1}{2\gamma} (e^{2\gamma t} - 1) \right]$   
 $= \frac{1}{2\gamma} (1 - e^{-2\gamma t})$



at  $t=0$  the velocity is well defined (the variance is zero) as time goes on the variance in the velocity distribution increases until it reaches  $\frac{1}{2\gamma}$  in the long time limit.

⑨  $N(x,t) = (A_0 + A_1 \cos \omega_R t) E_0 \cos \omega t + E_0 \cos \omega t + E_0 \cos \omega t$   
 $N(x,t) = A_0 E_0^2 \cos \omega t \cos \omega t \cos \omega t + A_1 E_0^2 \cos \omega t \cos \omega t \cos \omega t \cos \omega t$   
 $= A_0 E_0^2 [\cos^3 \omega t + 2 \cos \omega t] + A_1 E_0^2 [\cos(\omega - \omega_R)t + \cos(\omega + \omega_R)t + \cos(\omega - \omega_R)t + \cos(\omega + \omega_R)t]$

Resonance  
 $\omega = \omega_R$   
 $\omega = \omega_R$   
 $\omega = \omega_R$   
 $3\omega = \omega_R$

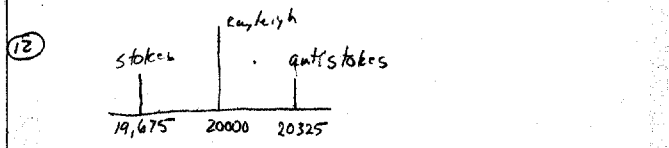
Process  
3rd harmonic growth  
DHW  
CSRS  
CARS

⑩  $\frac{N}{V} \rightarrow N(x) = N_0 e^{-\beta mgx}$   
 $\frac{N(x) kT}{V} = \frac{N(x) kT}{V} = \frac{N(x) kT}{V} e^{-\beta mgx}$   
 $P(x) = P_0 e^{-\beta mgx}$  ✓  
 $P(10km) = (1atm) e^{-\frac{(9.8 \frac{m}{s^2})(10,000m)}{(1.38 \times 10^{-23} J/K)(300K)}} =$

⑪  $\Delta = \frac{1}{\sqrt{2\pi NkT}}$

The "quantumness" goes down with increasing temp

Superfluidity and superconductivity occur at low temps.



22-141 50 SHEETS  
22-142 100 SHEETS  
22-143 150 SHEETS  
22-144 200 SHEETS

13)  $v^{(4)} = \begin{bmatrix} 32 \\ 18 \\ 32 \\ 38 \end{bmatrix}$   $v^{(5)} = \begin{bmatrix} 102 \\ 62 \\ 102 \\ 120 \end{bmatrix}$

16)

AA	AB	AC	AD
BA	BB	BC	BD
CA	CB	CC	CD
DA	DB	DC	DD
3	2	3	4

17)  $T_r[M] = 4 = W \checkmark$   $T_r[M^2] = 12 = W \checkmark$

18)  $\frac{S}{N} = k \ln W = k \ln \lambda_{max}$   $\lambda_{max} = 3.17$   
 $\frac{S}{N} = k \ln 3.17 = 1.153 k$

19)  $T_r[M^4] = 104$   $\frac{S}{N} = \frac{k \ln 104}{4} = 1.161 k$   
 error  $\frac{1.161 - 1.153}{1.161} = 0.68\%$

20)  $v_1 = \begin{bmatrix} 1 \\ 2 \\ 3 \end{bmatrix}$   $v_2 = \begin{bmatrix} 1 \\ 3 \\ 6 \\ 10 \end{bmatrix}$   $v_3 = \begin{bmatrix} 1 \\ 4 \\ 10 \\ 20 \end{bmatrix}$   $v_4 = \begin{bmatrix} 1 \\ 5 \\ 15 \\ 35 \end{bmatrix}$

21)

AAA	ABB	ABC	ABD
1 ✓	BBB	ACC	ACD
	3 ✓	BBC	ABD
		CCB	BCD
		6 ✓	BCD
			3DD
			6DD
			10 ✓

22)  $\frac{S}{N} = k \ln \lambda_{max}$ ,  $\lambda_{max} = 1$   $\frac{S}{N} = k \ln 1 = 0$

As  $N \rightarrow \infty$  chains that end with an infinite number of D's over which all else.