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Course 565/665 Lecture Number ______ Date 2/10/03

Lecturer Dr. Silvia Caragnero Note Taker Eric Fulmer

LAST TIME

$W \propto E$ When systems take up energy ie heat, it increases its multiplicity.

Example

* System A, System B } Each composed of 10 distinguishable particles.

$U_A = 2$, $W_A = \frac{10!}{8!\,2!} = 45$

$U_B = 4$, $W_B = \frac{10!}{6!\,4!} = 210$

$U_{Total} = U_A + U_B$

$W_{Total} = W_A W_B$

Lets think of System B as "Hot" and System A as "Cold".

When $U_A = 2$, $U_B = 4$, $W_{Total} = W_A \cdot W_B = 45 \cdot 210$
$= 9{,}450$

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$U_B \quad 4 \rightarrow 3$

$U_A \quad 2 \rightarrow 3$

$$W_A = W_B = \frac{10!}{3!\,7!}$$

$$W_{Total} = W_A \cdot W_B = 14{,}400$$

W_{Total} has <u>increased</u>.

<u>Alternatively</u>:

$U_B \quad 4 \rightarrow 5$

$U_A \quad 2 \rightarrow 1$

$$W_A = \frac{10!}{9!\,1!} \qquad W_B = \frac{10!}{5!\,5!}$$

$$W_{Total} = 2{,}520$$

W_{Total} has <u>decreased</u>.

Statistically, we see that the system will change to the state with the highest multiplicity. For a large enough N, this highest multiplicity state becomes the only state observed since the other states have a much much lower probability of being observed.

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Example

A 10 distinguishable particles

B 4 distinguishable particles

Let $U_A = 2$ $U_B = 2$

$$W_{Total} = W_A \cdot W_B = \frac{10!}{2!\,8!} \cdot \frac{4!}{2!\,2!} = 270$$

U_B $2 \to 1$ Energy transfer has occured.

U_A $2 \to 3$

$$W_{Total} = W_A \cdot W_B = \frac{10!}{3!\,7!} \cdot \frac{4!}{1!\,3!} = 480$$

T is a very interesting property that is related to energy, but T is definitly not the same as heat or internal energy.

[See Chaptr 12 for more.]

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Chapter 5

Math Tools – Multivariable Calculus

$y = f(x)$ y is the dependent variable
x is the independent variable.

$y = f(x_1, x_2)$
$z = f(x, y)$
These are functions of more than one independent variable. These are Multivariate Functions (MF)

$$z = (x - x_0)^2 + (y - y_0)^2$$ 3D Quadratic function.

M.F.'s of 2 independent variables describe 3D Surfaces.

Partial Derivatives

Given "f",

$$\left(\frac{\partial f}{\partial x}\right)_y \equiv \lim_{\Delta x \to 0} \frac{f(x + \Delta x, y) - f(x, y)}{\Delta x}$$

$$\left(\frac{\partial f}{\partial y}\right)_x \equiv \lim_{\Delta y \to 0} \frac{f(x, y + \Delta y) - f(x, y)}{\Delta y}$$

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Example $P = \frac{RT}{V}$ $R \equiv$ gas constant

P is a function of T and V, or $P = P(T, V)$.

$$\left(\frac{\partial P}{\partial V}\right)_T = \frac{-RT}{V^2} \qquad \left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V}$$

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_T = \frac{2RT}{V^3} \qquad \left(\frac{\partial^2 P}{\partial T^2}\right)_V = 0$$

$$\left(\frac{\partial^2 P}{\partial T\,\partial V}\right)_{T,V} = \left(\frac{\partial}{\partial T}\left(\frac{\partial P}{\partial V}\right)_T\right)_V = \left(\frac{\partial}{\partial T}\left(\frac{-RT}{V^2}\right)\right)_V = \frac{-R}{V^2}$$

$$\left(\frac{\partial^2 P}{\partial V\,\partial T}\right)_{V,T} = \left(\frac{\partial}{\partial V}\left(\frac{\partial P}{\partial T}\right)_V\right)_T = \left(\frac{\partial}{\partial V}\left(\frac{R}{V}\right)\right)_T = \frac{-R}{V^2}$$

Thus, the order of the differentiation does not matter. The same result is obtained from both methods. Therefore,

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

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Total Differentials

Given $f(x)$, evaluate f at a, or $f(a)$.

$$\Delta f = f(x) - f(a) = f'(a)\,\Delta x + \frac{1}{2} f''(a)\,\Delta x^2 + \frac{1}{6} f'''(a)\cdot \Delta x^3 + \dots$$

Where $f(x)$ is expanded about point "a" with a Taylor Series Expansion and $\Delta x = (x-a)$.

for $x \approx a$, thus $dx = (x-a)$ becomes a very small #.

$$df = f'(a)\,dx + \frac{1}{2} f''(a)\,dx^2 + \frac{1}{6} f'''(a)\,dx^3 + \dots$$

and $dx^2, dx^3 \ll dx$. Thus, these can be ignored or approximated to equal zero.

$$df = f'(a)\,dx$$

For $f(x,y)$: $\Delta f = f(x,y) - f(a,b)$

$x = a$
$y = b$