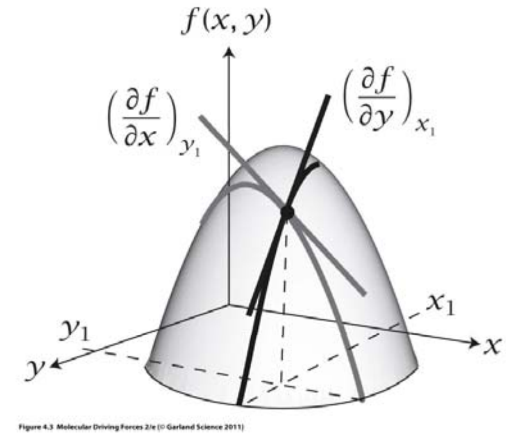
CHAPTER 4 MATH TOOLS

$$f = f(x, y)$$

dependent — independent variables



partial derivatives

$$\left(\frac{\partial f}{\partial x}\right)_y = \frac{f(x+\Delta x, y) - f(x, y)}{\Delta x}, \qquad \left(\frac{\partial f}{\partial y}\right)_x = \frac{f(x, y+\Delta y) - f(x, y)}{\Delta y}$$

held constant

Example:

$$p = p(V, T) = \frac{RT}{V}$$ ideal gas

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

$$\frac{\partial^2 p}{\partial V^2} = \frac{2RT}{V^3}, \qquad \left(\frac{\partial^2 p}{\partial T^2}\right)_V = 0, \qquad \frac{\partial^2 p}{\partial p \partial T} = -\frac{R}{V^2}$$

order of derivatives does not matter

Taylor series in one independent variable

$$\Delta f = f(x) - f(a) = \left(\frac{df}{dx}\right)_{x=a} \Delta x + \frac{1}{2}\left(\frac{d^2 f}{dx^2}\right)_{x=a} \Delta x^2 + \frac{1}{6}\left(\frac{d^3 f}{dx^3}\right) \Delta x^3 + \dots$$

where $\Delta x = (x - a) \to dx$ when the step is small

$$df = \left(\frac{df}{dx}\right)_{x=a} dx$$

Now extend to a function of two variables

$$\Delta f = f(x,y) - f(a,b) = \left(\frac{\partial f}{\partial x}\right)_y \Delta x + \left(\frac{\partial f}{\partial y}\right)_x \Delta y + \frac{1}{2}\left[\left(\frac{\partial^2 f}{\partial x^2}\right)\Delta x^2 \Delta y^2 + 2\frac{\partial^2 f}{\partial x \partial y}\Delta x \Delta y + \left(\frac{\partial^2 f}{\partial y^2}\right)\Delta y^2\right] + \dots$$

so for small changes

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy$$

readily generalized to more variables

$\left(\frac{\partial f}{\partial x}\right)_y$ means the derivative with respect to *x* is taken with *y* held constant and then it is evaluated at *x = a, y = b*

How to find extrema

consider $f = x^2 + b$

$$\frac{df}{dx} = 2x = 0$$

$$\Rightarrow x^* = 0$$

$$\left.\frac{d^2 f}{dx^2}\right|_{x=x^*} = 2 > 0$$

$\Rightarrow$ minimum

second derivative gives curvature

Now consider $f(x,y)$

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dx$$

Need both derivatives to vanish to have a stationary point

$$(\partial f / \partial x)_y = 0, \qquad (\partial f / \partial y)_x = 0$$

In general, for $f(x_1, x_2, \ldots x_t)$ need $\left(\frac{\partial f}{\partial x_i}\right)_{x_{j \neq i}} = 0$ for extremum

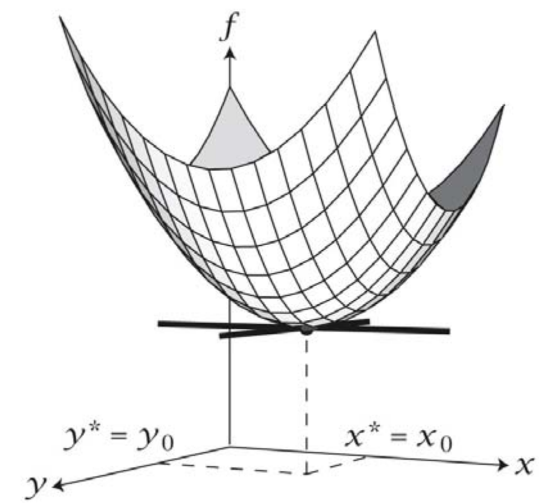


Figure 4.6 Molecular Driving Forces 2/e (© Garland Science 2011)

Example: $f\left(x-x_0\right)^2+\left(y-y_0\right)^2$

$$\left(\frac{\partial f}{\partial x}\right)_y = 2\left(x-x_0\right) \Rightarrow x^* = x_0$$

$$\left(\frac{\partial f}{\partial y}\right)_x = 2\left(y-y_0\right) \Rightarrow y^* = y_0$$

$\left(x_0, y_0\right)$ stationary point

$$\left(\frac{\partial^2 f}{\partial x^2}\right)_{x^*,y^*} \rightarrow 2, \quad \left(\frac{\partial^2 f}{\partial y^2}\right)_{x^*,y^*} \rightarrow 2$$

possible minumum

In general, cannot tell what sort of extremum one has from these two derivatives alone

$$M = \begin{pmatrix} \left(\frac{\partial^2 f}{\partial x^2}\right)_{x^*y^*} & \left(\frac{\partial^2 f}{\partial x \partial y}\right)_{x^*y^*} \\ \left(\frac{\partial^2 f}{\partial x \partial y}\right)_{x^*y^*} & \left(\frac{\partial^2 f}{\partial y^2}\right)_{x^*y^*} \end{pmatrix}$$

Hessian matrix

$$\xrightarrow{\text{eigenvalues}} \left(\frac{\partial^2 f}{\partial x^2}\right)_{x^*y^*} \left(\frac{\partial^2 f}{\partial y^2}\right)_{x^*y^*} - \left(\frac{\partial f}{\partial x \partial y}\right)^2_{x^*y^*}$$

$f_{xx}, f_{yy} > 0, M > 0$	minimum
$f_{xx}, f_{yy} < 0, M > 0$	maximum
$M < 0$	saddle point
$M = 0$	inconclusive

for problem above $M = 4 \Rightarrow$ minimum

Consider $f = x^2 + y^2 - 4xy$

$$\left(\frac{\partial f}{\partial x}\right)_y = 2x - 4y \qquad \left(\frac{\partial f}{\partial y}\right)_x = 2y - 4x$$

set derivatives = 0 $\Rightarrow$

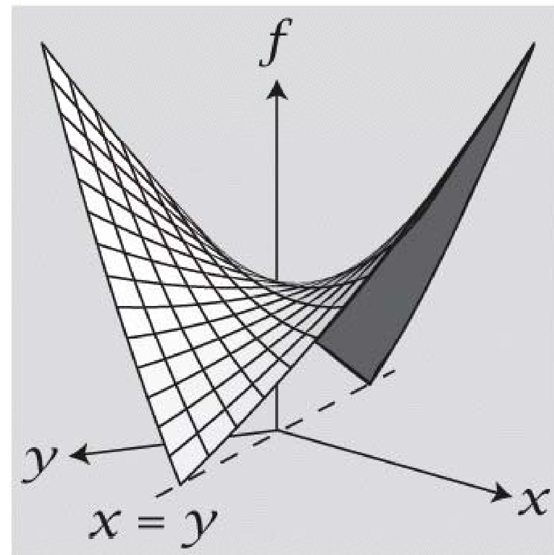
$$x = 2y, \qquad y = 2x \Rightarrow (x^*, y^*) = (0,0)$$

$$\left(\frac{\partial^2 f}{\partial x^2}\right) = 2, \qquad \left(\frac{\partial^2 f}{\partial y^2}\right) = 2, \qquad \frac{\partial^2 f}{\partial x \partial y} = -4$$

$$M = 4 - 16 = -12$$

saddle point

(a) $f(x, y) = x^2 + y^2 - 4xy$



Now consider functions subject to constraints

e.g., find extrema of *f(x,y)* subject to a constraint *g(x,y)*

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy, \quad g(x,y) = x - y = 0 \Rightarrow x = y$$

$$dg = \left(\frac{\partial g}{\partial x}\right)_y dx + \left(\frac{\partial g}{\partial y}\right)_x dy \Rightarrow dx - dy = 0$$

$$\Rightarrow \quad dx = dy$$

$$\Rightarrow \left(\frac{\partial f}{\partial x}\right)_y = \left(\frac{\partial f}{\partial y}\right)_x$$

⟵ finds extremum of *f* along line *x=y*

Example: find minimum of $f = x^2 + y^2$ subject to $g = x + y = 6$

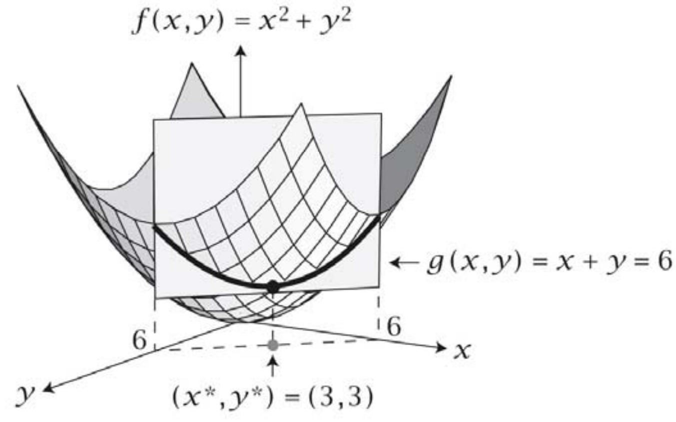


Figure 4.8 Molecular Driving Forces 2/e (© Garland Science 2011)

$$\left(\frac{\partial f}{\partial x}\right)_y = 2x, \quad \left(\frac{\partial f}{\partial y}\right)_x = 2y \quad \Big| \quad \left(\frac{\partial g}{\partial x}\right)_y = 1, \quad \left(\frac{\partial g}{\partial y}\right)_x = 1$$

$$dg = dx + dy = 0$$
$$dx = -dy$$

$$df = 2xdx + 2ydy$$
$$= 2xdx - 2ydy = (2x - 2y)dx$$

$$set = 0 \Rightarrow x^* = y^*$$

$$y^* = 6 - x^* \rightarrow x^* = 6 - x^* \qquad x^* = 3, \quad y^* = 3$$

minimum is at (3,3)

Method of Lagrange multipliers – More systematic approach

$$\Lambda = f - \lambda(g - c)$$

$$d(f - \lambda g) = \sum\left[\left(\frac{\partial f}{\partial x_i}\right) - \lambda\left(\frac{\partial g}{\partial x_i}\right)\right]dx_i = 0$$

λ is the Lagrange multiplier

so back to previous problem

$$d(f - \lambda g) = (2x - \lambda)dx + (2y - \lambda)dy = 0$$

$$\Rightarrow 2x = \lambda, \quad 2y = \lambda \Rightarrow x = y \Rightarrow (x^*, y^*) = (3^*, 3)$$

find the minimum of

$$f = 50 - (x-3)^2 - (y-6)^2$$

$$d(f - \lambda g) = \left(-2(x-3) + \lambda\right)dx + \left(-2(y-6) - \lambda\right)dy = 0$$

subject to $g = y - x = 0$

$$2(x-3) = \lambda$$

$$2(y-6) = -\lambda$$

$$y - 6 = -x + 3$$

$$y = -x + 9$$

$$\Rightarrow 2y = 9 \qquad y^* = 4.5, \quad x^* = 4.5$$

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if 2 independent variables (x_1, x_2) and 2 constraints (g, h)

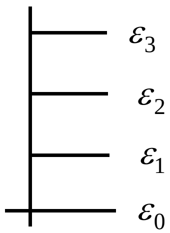
$$\frac{\partial f}{\partial x_1} - \lambda \frac{\partial g}{\partial x_1} - \beta \frac{\partial h}{\partial x_1} = 0$$

$$\frac{\partial f}{\partial x_2} - \lambda \frac{\partial g}{\partial x_2} - \beta \frac{\partial h}{\partial x_2} = 0$$

Easy to generalize to any number of variables and constraints

Why are the Lagrange multipliers going to be important to us?

recall that many of the systems of interest to us have energy levels



Suppose we want to distribute three particles among the levels, giving a total energy ε'. Then not all distributions are possible. We can only have those where $E_{tot} = \varepsilon'$. This is a constraint

Integrating multivariate functions

- state function (independent on path)
- path dependent

Consider two routes between cities *A* and *B*

the change in altitude between *A* and *B* is independent of the path
the distance traveled is path dependent

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small changes in a function can be written as

$$t(x,y)\,dx + s(x,y)\,dy$$

A state function is a function that obeys

$$df = s\,dx + t\,dy = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy$$

$xy^2\,dx + x\,dy$ is not a state function

$$f = xy, \quad \left(\frac{\partial f}{\partial x}\right)_y = y, \quad \left(\frac{\partial f}{\partial y}\right)_x = x \quad \longleftarrow$$

$df = y\,dx + x\,dy$ is a state function

For a state function

$$\int_{y_A}^{y_B}\int_{x_A}^{x_B}\left(sdx+tdy\right)=f\left(x_B,y_B\right)-f\left(x_A,y_A\right)=f_B-f_A \quad \longleftarrow$$ need only end points

If f is state function $\Rightarrow$ df an exact differential

y^2dx+x^2dy is an inexact differential $\neq d\left[f\left(x,y\right)\right]$

Euler reciprocal relationship test

$$\frac{\partial^2 f}{\partial x\partial y}=\frac{\partial^2 f}{\partial y\partial x}$$ for a state function

So given $s\left(x,y\right)dx+t\left(x,y\right)dt$

we need to check if $\dfrac{\partial s}{\partial y}=\dfrac{\partial t}{\partial x}$

if so $s=\dfrac{\partial f}{\partial x},t=\dfrac{\partial f}{\partial y}$

and $sdx+tdy$ is an exact differential

Chain rule

$f\left[g(x)\right] \leftarrow$ a function of a function

Consider $f = f\left(x(u), y(u), z(u)\right)$ | x, y, z are functions of u

$$df = \left(\frac{\partial f}{\partial x}\right)_{y,z} dx + \left(\frac{\partial f}{\partial y}\right)_{x,z} dy + \left(\frac{\partial f}{\partial z}\right)_{x,y} dz$$

$$\frac{df}{du} = \left[\left(\frac{\partial f}{\partial x}\right)_{y,z}\left(\frac{dx}{du}\right) + \left(\frac{\partial f}{\partial y}\right)_{x,z}\frac{dy}{du} + \left(\frac{\partial f}{\partial z}\right)_{x,y}\frac{dz}{du}\right]$$

$\frac{d}{du}$: differentiation when function depends on single variable

$\frac{\partial}{\partial x}$: partial differentiation when function depends on two or more variables

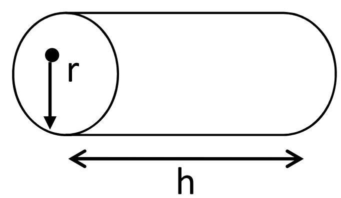
Suppose height $z = x^2$ and $u = mgz$

$$\Rightarrow u = u\big(z(u)\big)$$

$$\frac{du}{dx} = \frac{\partial u}{\partial z}\frac{dz}{dx} = 2mgx$$

Reshaping a cylinder, keeping the volume constant

$$dV = \left(\frac{\partial V}{\partial r}\right)_h dr + \left(\frac{\partial V}{\partial h}\right)_r dh = 2\pi rhdr + \pi r^2 dh$$



Volume: $V = \pi r^2 h$

set = 0

$$2hdr = -rdh \Rightarrow \frac{dh}{dr} = -\frac{2h}{r}$$

$$\int_{h_1}^{h_2} \frac{dh}{h} = -2\int_{r_1}^{r_2} \frac{dr}{r} \rightarrow \ell n\left(\frac{h_2}{h_1}\right) = -2\ell n\left(\frac{r_2}{r_1}\right)$$

$$\Rightarrow \frac{h_2}{h_1} = \left(\frac{r_1}{r_2}\right)^2 \longrightarrow$$

if double radius, need to reduce *h* by ¼ to conserve volume