微分・積分と物理化学

切っても切れない仲

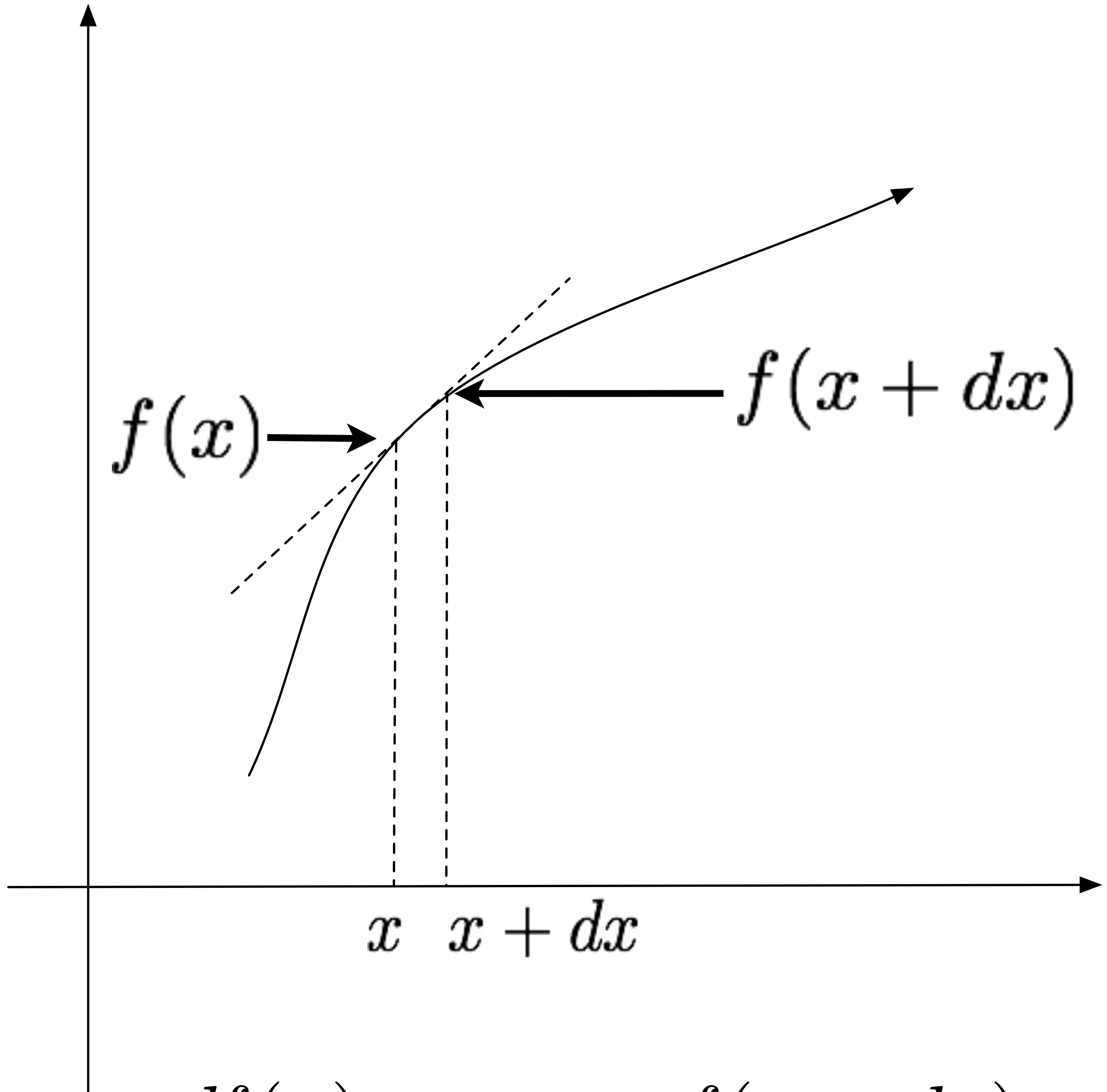
今さら公式憶える？
定義から導きましょう！！

…
物理化学で最も脅威を憶える点は，習ったことがないか，たとえ習ったとしても忘れてしまっている数学を遠慮なく使うことであろう。

…
物理化学の講義を何年もした経験から，物理化学のトピックを提示する前にそこで使う数学を復習するのが役に立つことが解った。

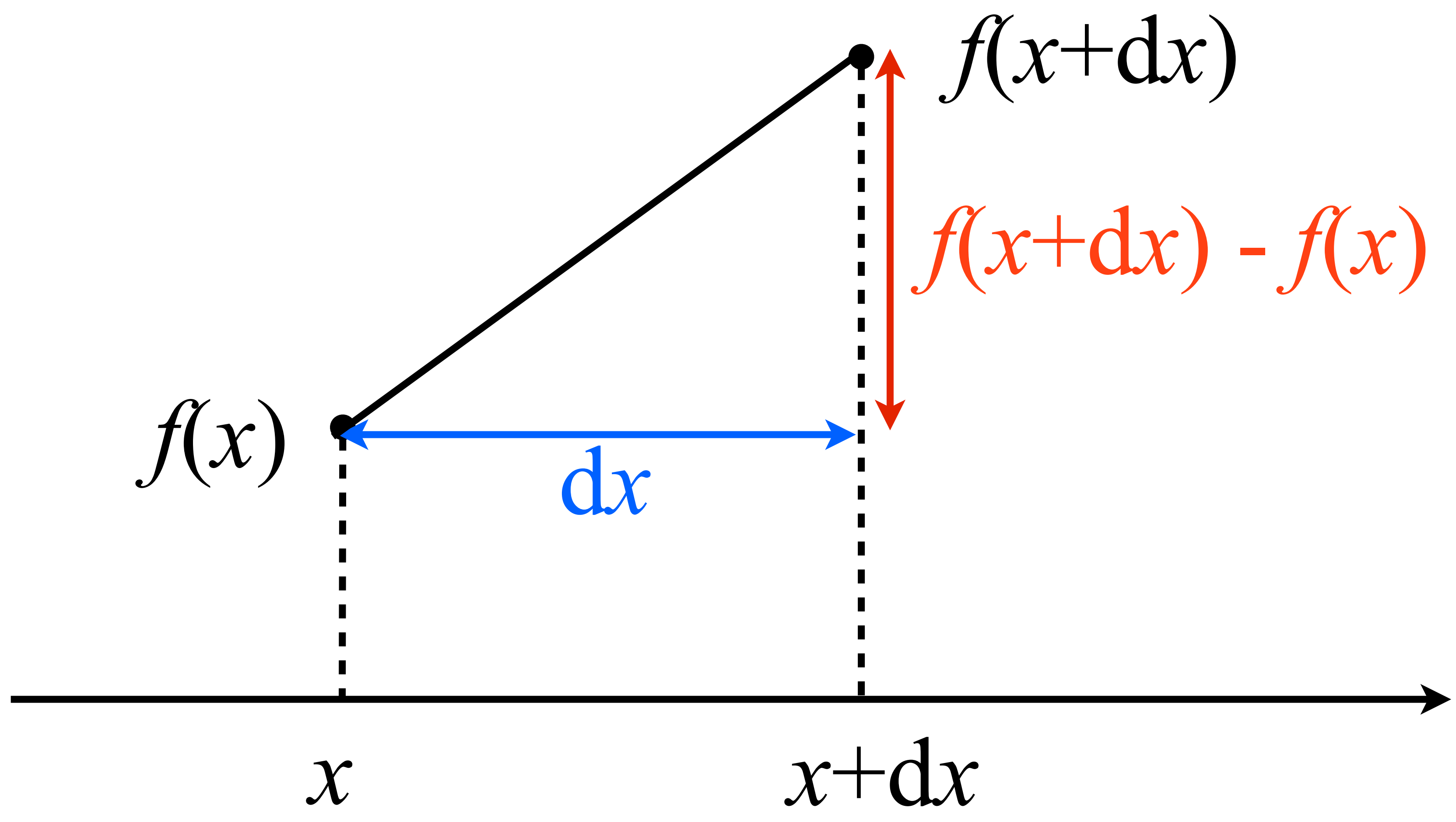
マッカリー・サイモン　物理化学　序

微分



$$
\begin{aligned}
f'(x) &= \frac{df(x)}{dx} = \lim_{dx\to 0}\frac{f(x+dx)-f(x)}{x+dx-x} \\
&= \lim_{dx\to 0}\frac{f(x+dx)-f(x)}{dx}
\end{aligned}
$$

例：$f(x) = A,\ f(x) = ax, f(x) = ax^2$



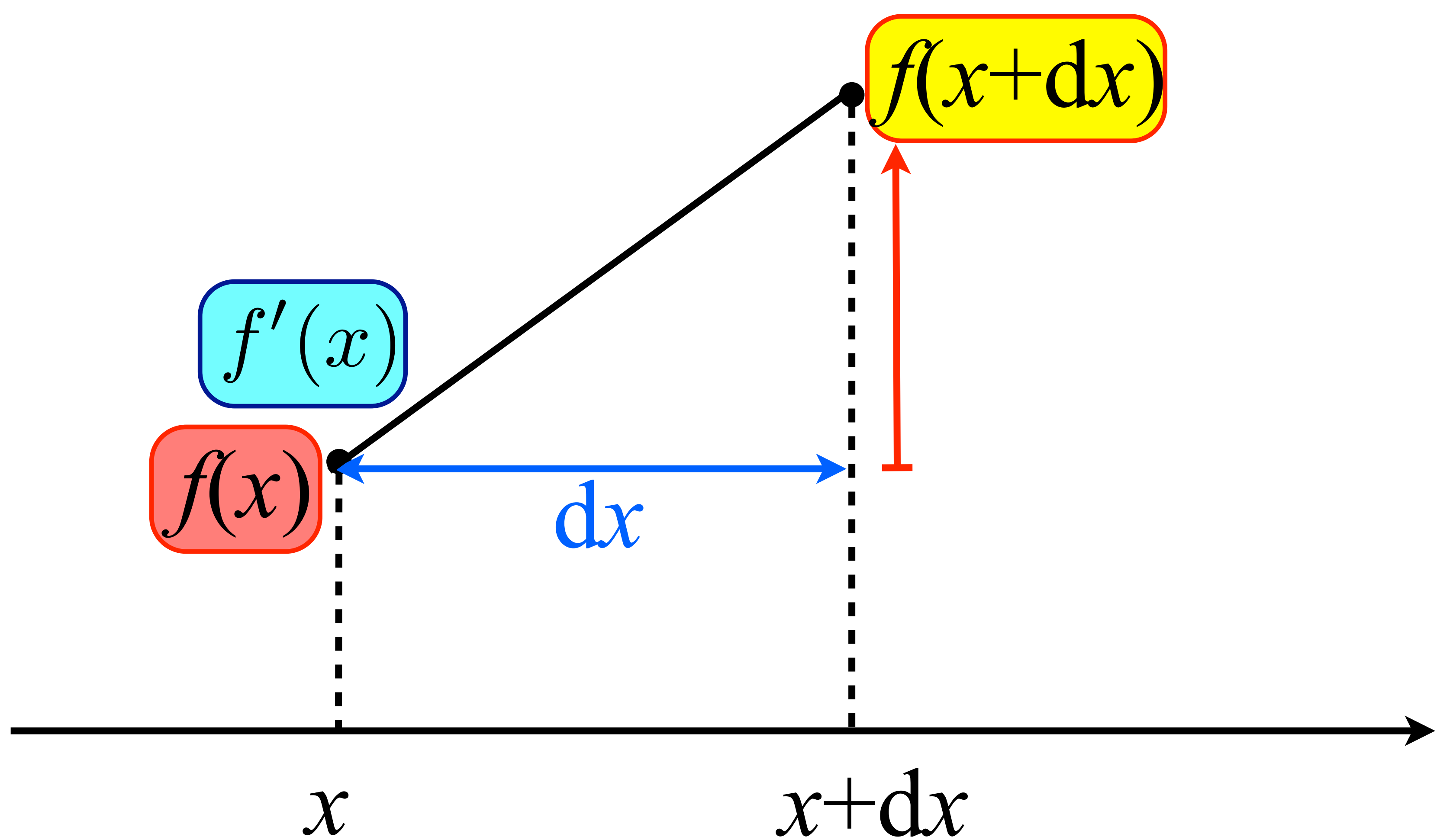
$$
\begin{aligned}
f'(x) &= \frac{df(x)}{dx} = \lim_{dx \to 0} \frac{f(x+dx) - f(x)}{x + dx - x} \\
&= \lim_{dx \to 0} \frac{\boxed{f(x+dx) - f(x)}}{\boxed{dx}}
\end{aligned}
$$

$$f'(x) = \lim_{dx \to 0} \frac{f(x+dx) - f(x)}{dx}$$

えいやっとをlimはずす

$$f(x+dx) \simeq f(x) + f'(x)dx$$

この関係は今後よく使います　　傾き×距離



偏微分

partial differentiation

$$\frac{\partial f(x,y)}{\partial x}, \ \frac{\partial f(x,y)}{\partial y}$$

∂は，ラウンド，デル，パーシャルとか呼ぶ

$f(x,y)$：
座標x,y
での標高

２変数関数

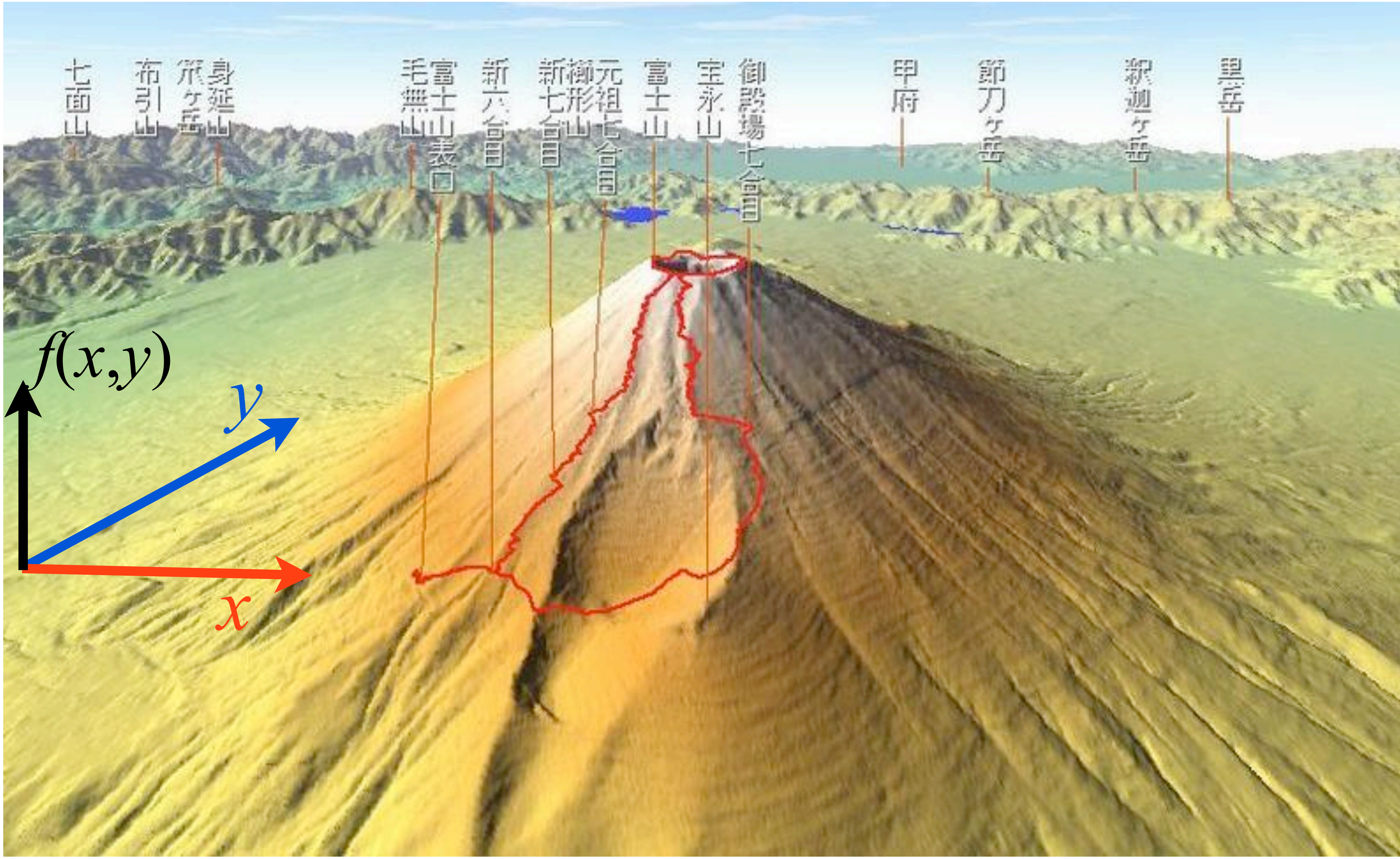
1 変数関数

$f(x)$:df /dx = 傾斜

2次元の絵での富士山

2変数関数

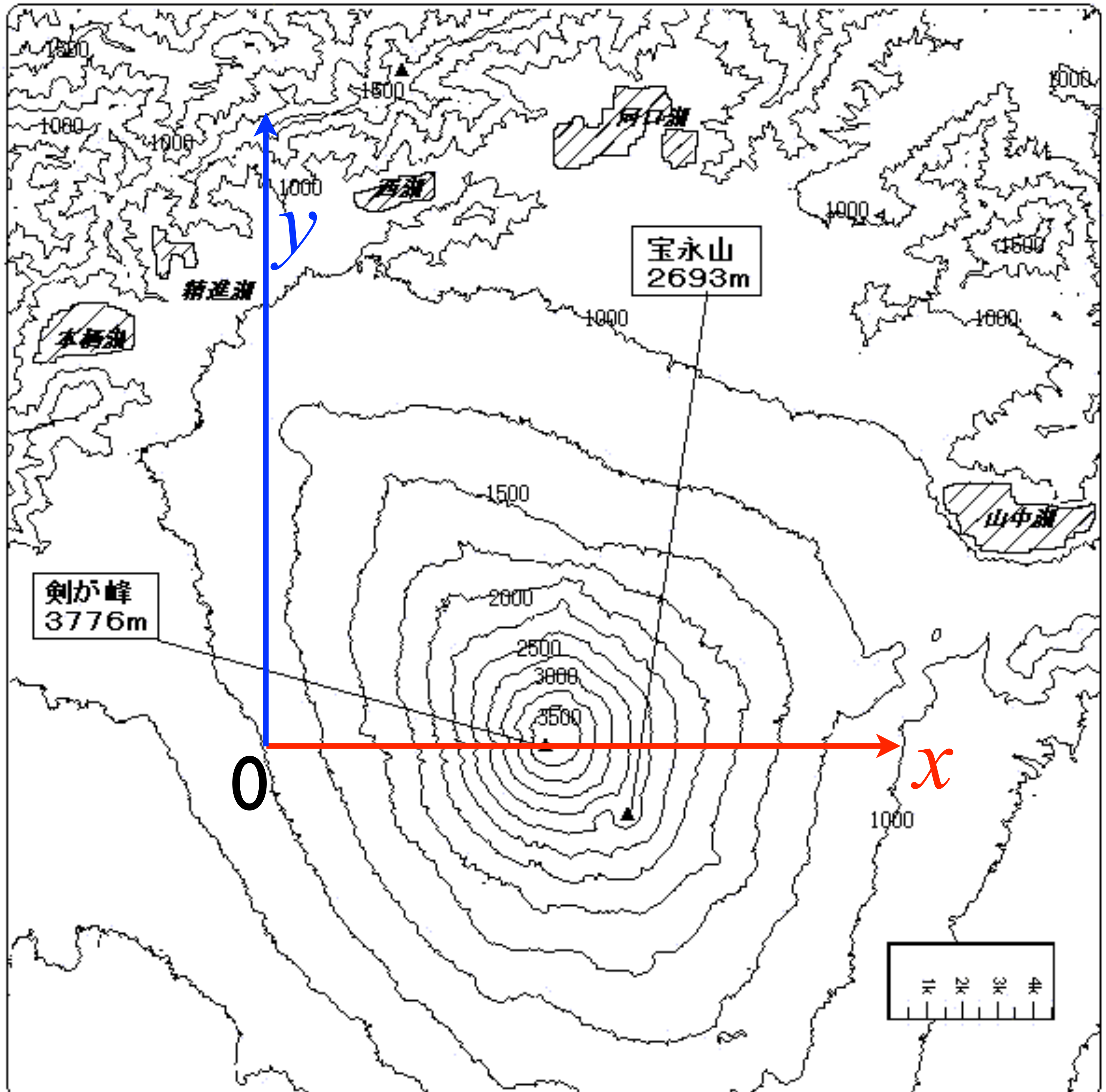
富士山



９合目からがおもろい！

地元タクシーのおっちゃんの名言：一度は登ってみなはれ，２度登る人はあほやけど！

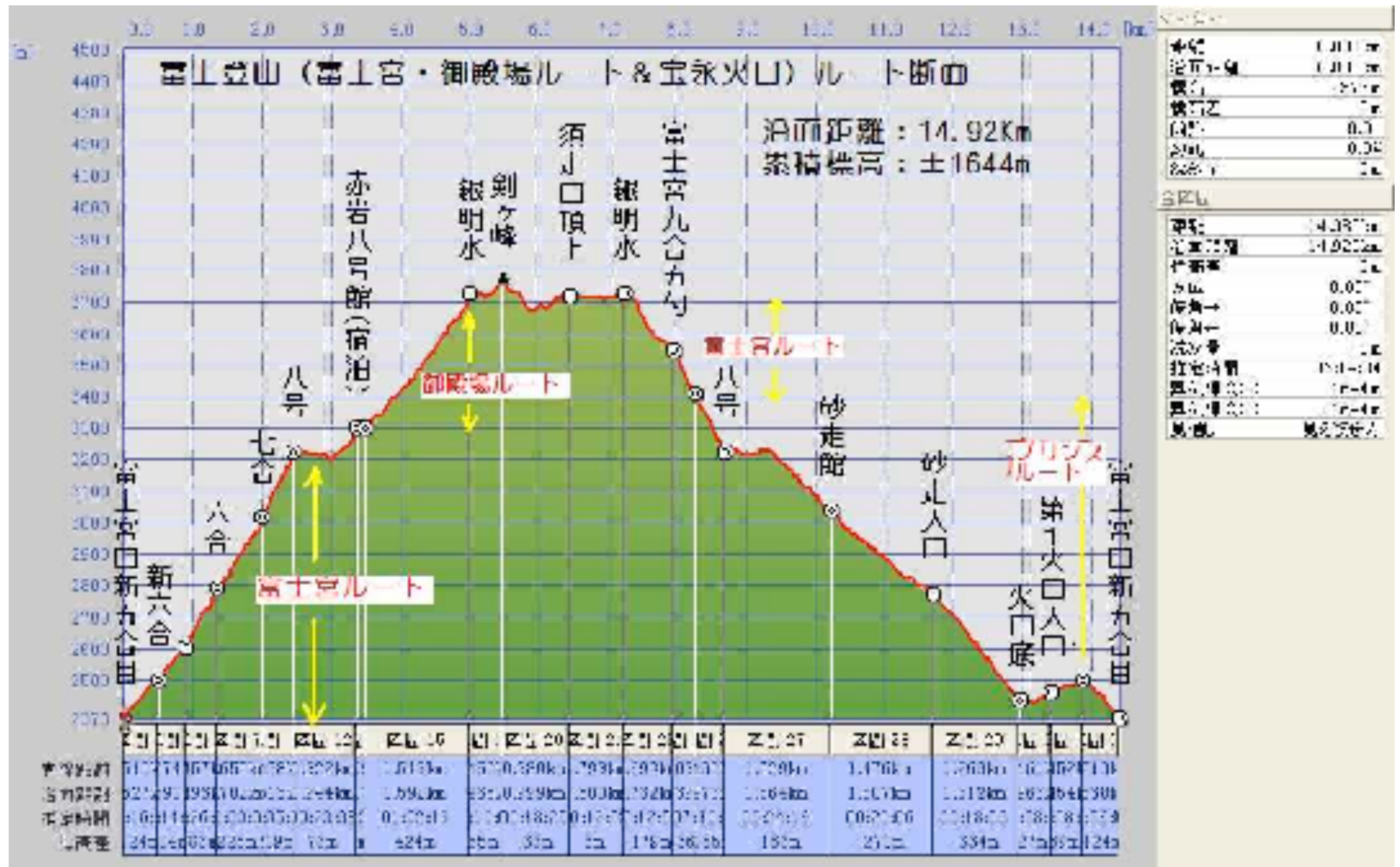
等高線図



標高：$f(x, y)$ 2変数関数

$y = 0$ での断面

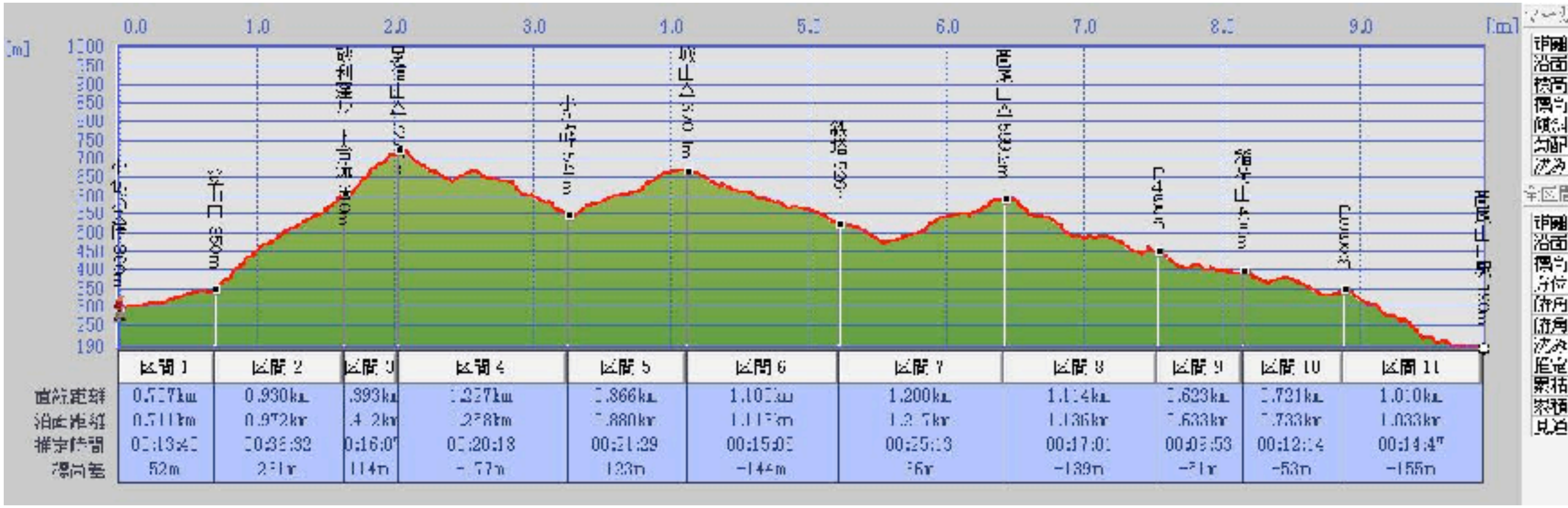
+ → 0 → -



その勾配

$$\left(\frac{\partial f}{\partial x}\right)_{y=0} = \lim_{dx \to 0} \frac{f(x+dx, y=0) - f(x, y=0)}{dx}$$

$x = 0$ での断面　　+ → 0 → -



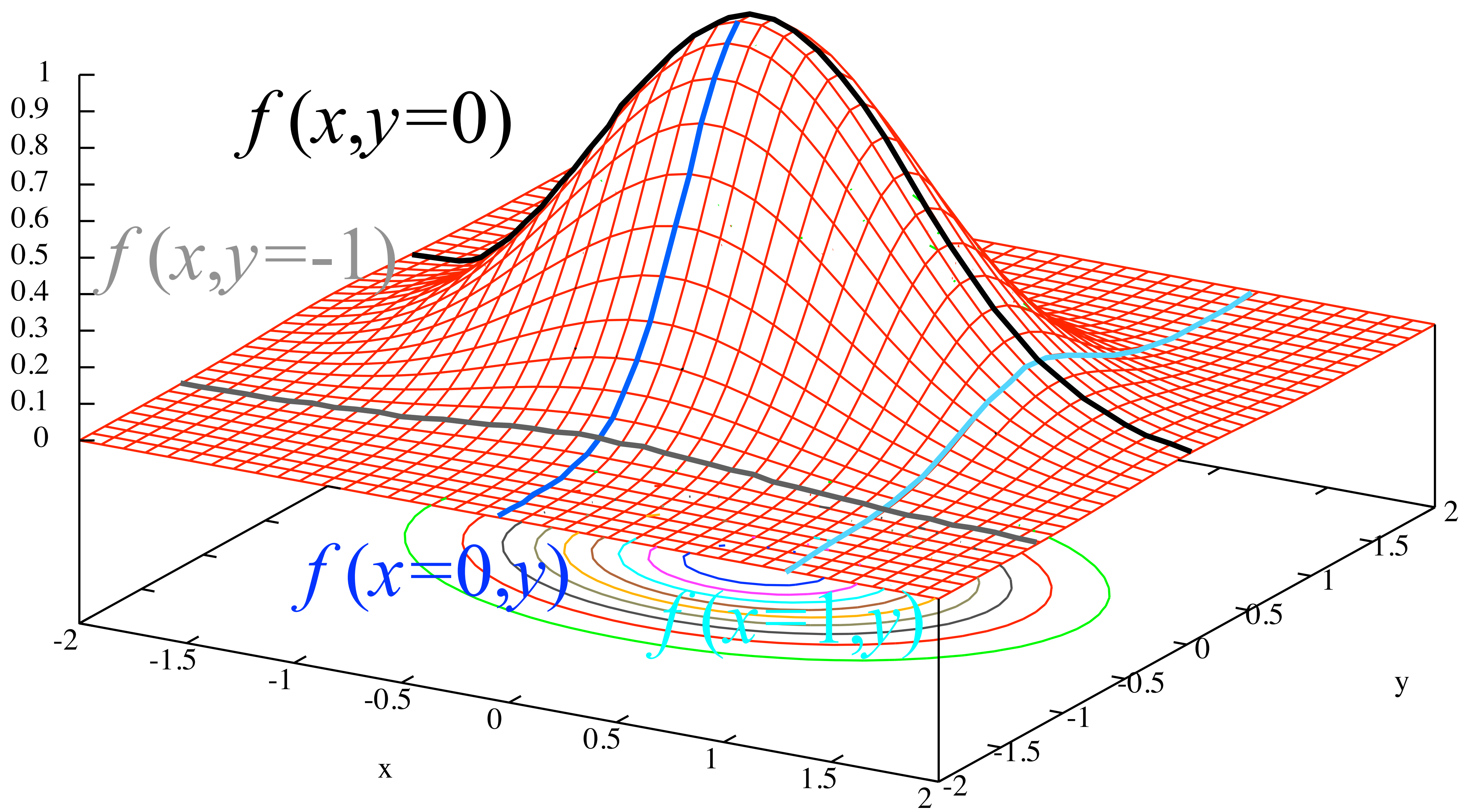
その勾配

$$\left(\frac{\partial f}{\partial y}\right)_{x=0} = \lim_{dy \to 0} \frac{f(x=0, y+dy) - f(x=0, y)}{dy}$$

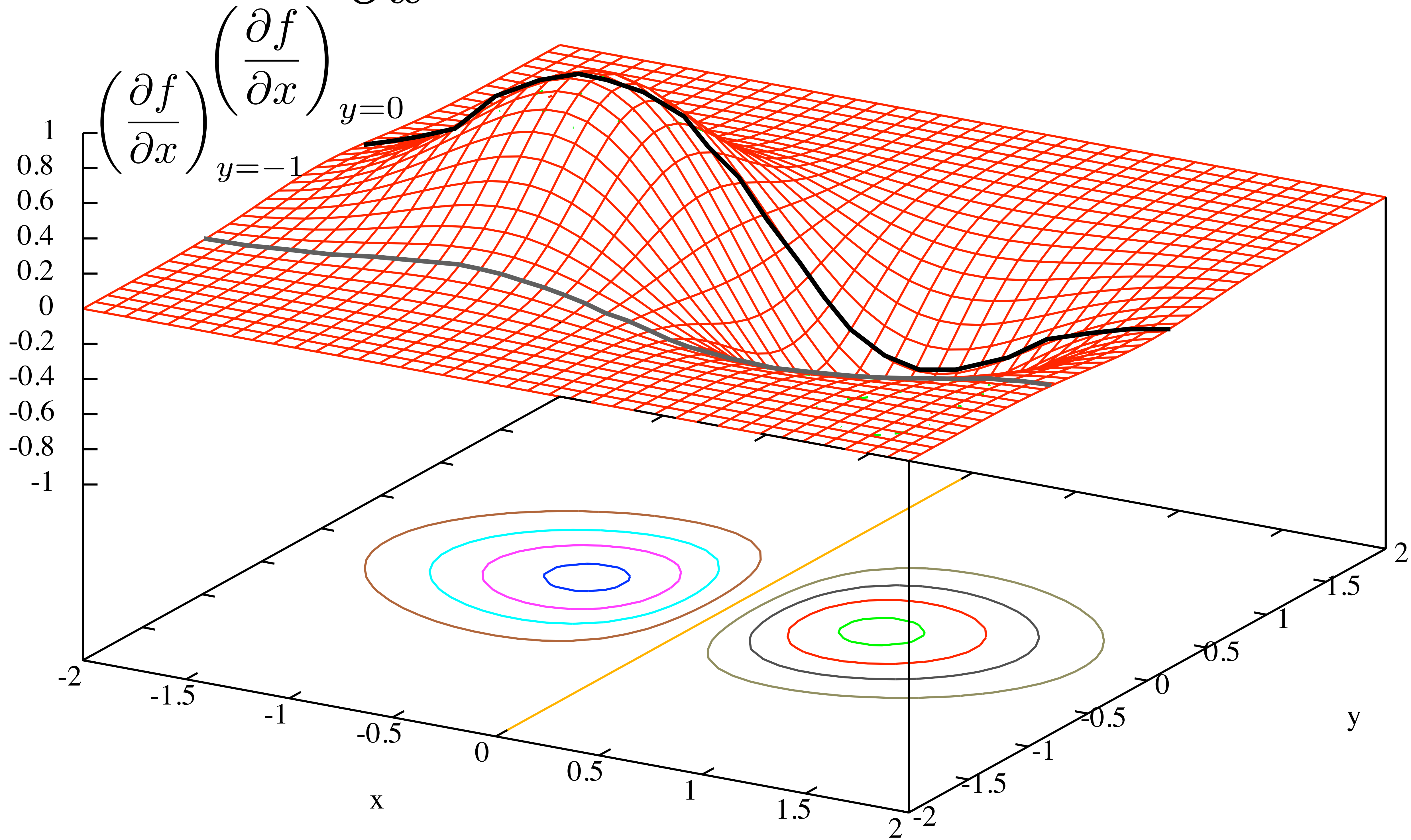
$\frac{\partial f}{\partial x}$ ：数学の技法としては,

yを定数と見なして,xだけで微分すればよい

例： $f(x,y) = \exp(-x^2-2y^2)$

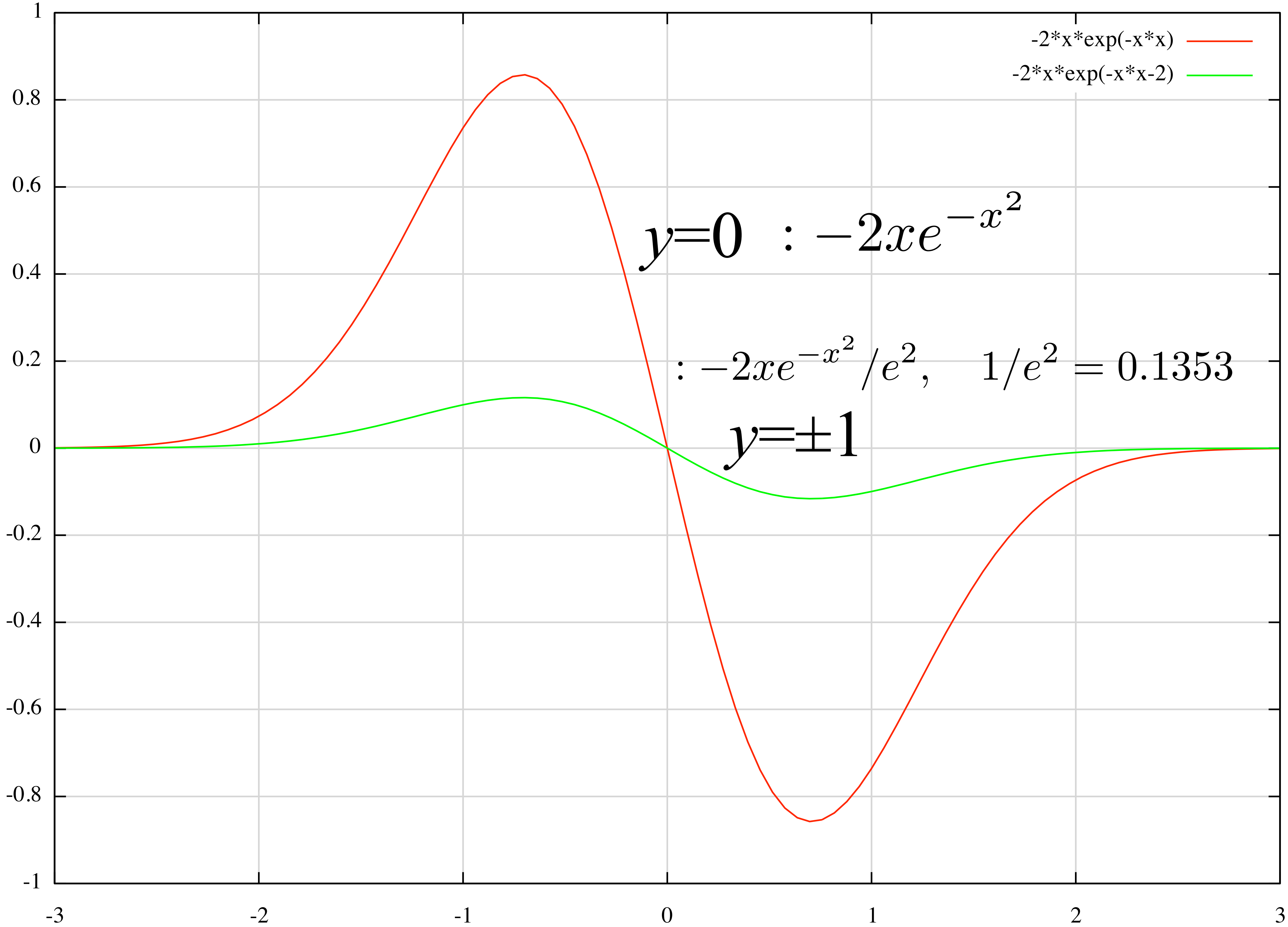


$$\frac{\partial f}{\partial x} = -2x\exp(-x^2 - 2y^2)$$

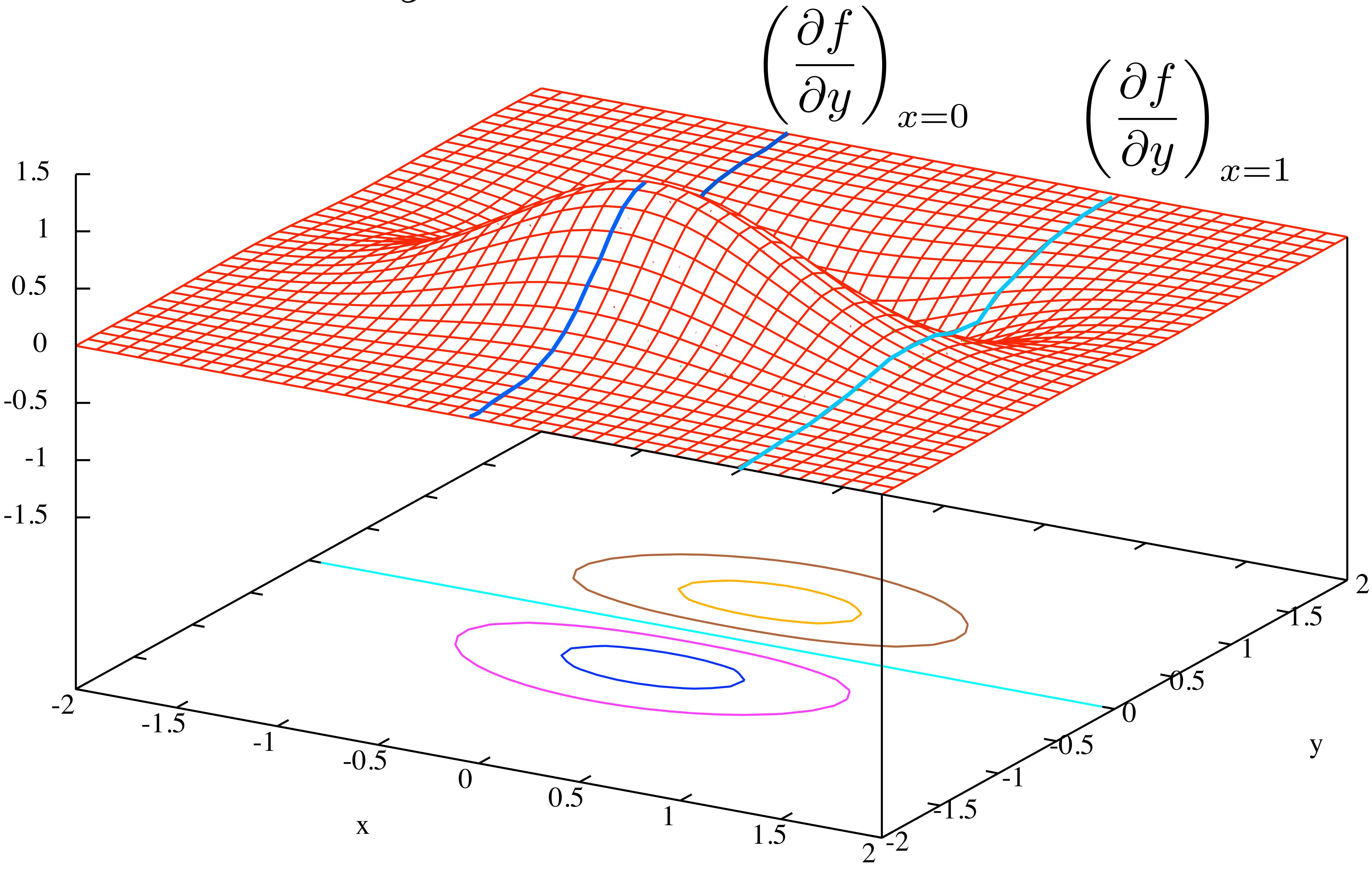


すべてのx,yで定義可能なことに注意

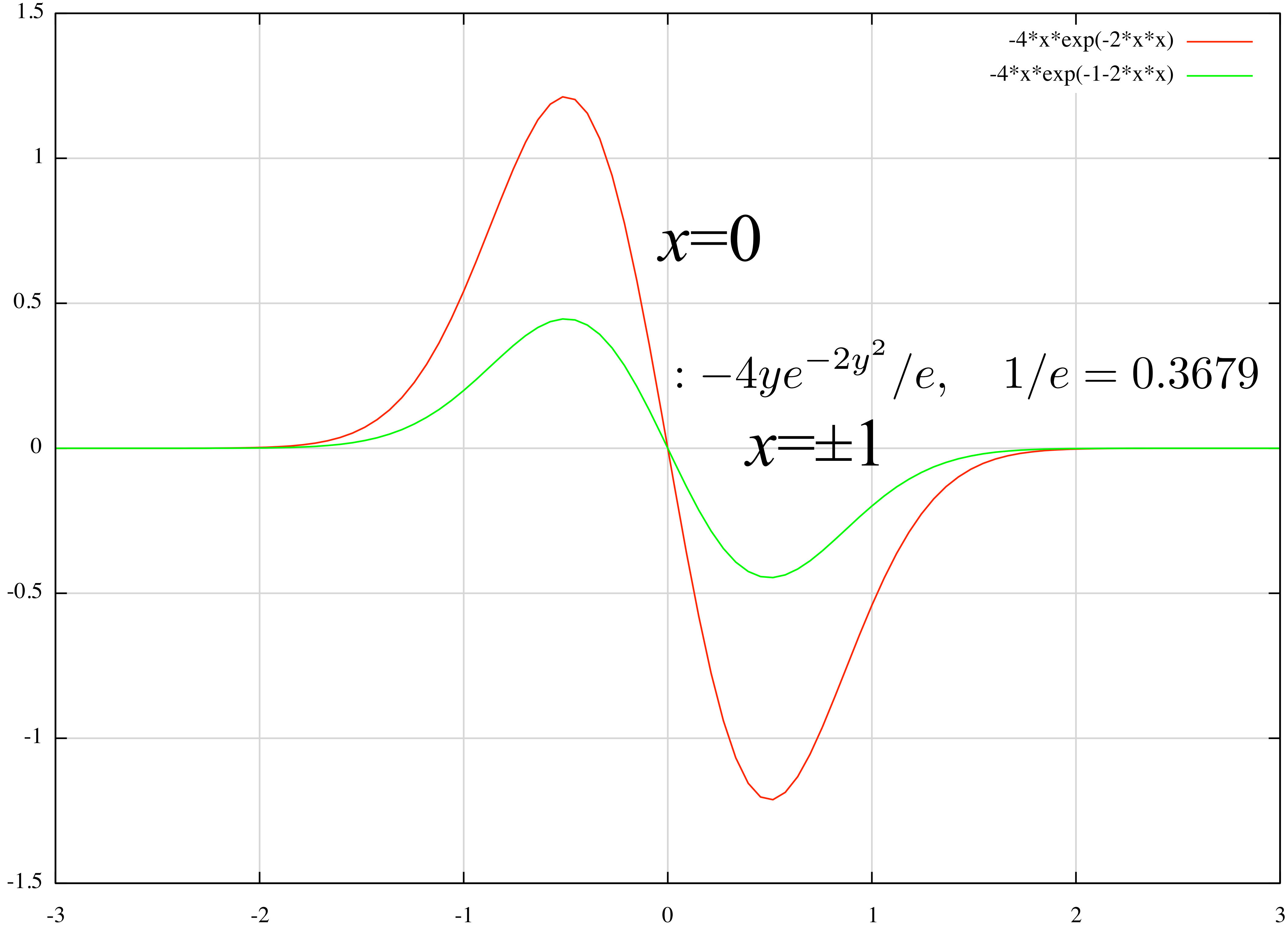
$$\frac{\partial f}{\partial x} = -2x\exp(-x^2 - 2y^2)$$



$$\frac{\partial f}{\partial y} = -4y\exp(-x^2 - 2y^2)$$



$$\frac{\partial f}{\partial y} = -4y\exp(-x^2 - 2y^2)$$



余談ですが

数式をグラフにする方法

0) 関数電卓で計算してグラフ用紙に
プロットする

時間がかかりすぎる！

数式をグラフにする方法

1）エクセル　おすすめしない

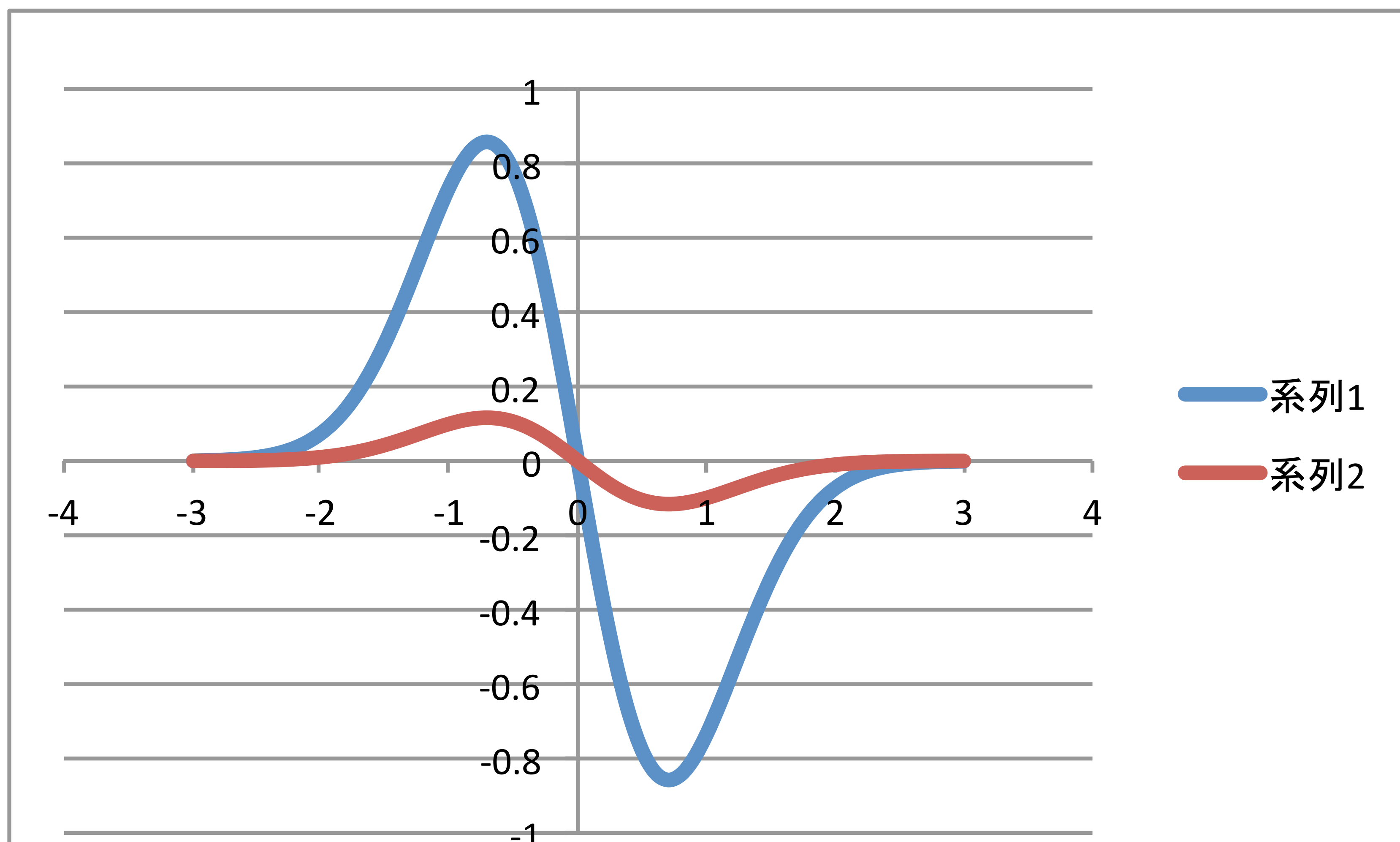
Aのカラムをつくる

Bのカラム　=-2*A1*EXP(-A1*A1)

Cのカラム　=-2*A1*EXP(-A1*A1-2)

３つのカラムを指定して,
グラフ・散布図・平滑線

	A	B	C
1	-3	0.000740459	0.00010021
2	-2.9	0.001291253	0.000174752
3	-2.8	0.002204547	0.000298353
4	-2.7	0.003684571	0.000498653
5	-2.6	0.006027992	0.0008158
6	-2.5	0.009652271	0.001306293
7	-2.4	0.015125336	0.002046992
8	-2.3	0.023192097	0.003138709
9	-2.2	0.034791038	0.004708455
10	-2.1	0.051051749	0.006909103
11	-2	0.073262556	0.009915009
12	-1.9	0.102797018	0.013912064
13	-1.8	0.140990022	0.019080925
14	-1.7	0.188959123	0.025572836
15	-1.6	0.247375169	0.033478589
16	-1.5	0.316197674	0.042792702
17	-1.4	0.394403579	0.05337672
18	-1.3	0.479750762	0.064927205
19	-1.2	0.568626621	0.076955245
20	-1.1	0.656034015	0.088784549
21	-1	0.735758882	0.099574137



数式をグラフにする方法

２）フリーソフトGNUPLOTを使う。センターにあり。

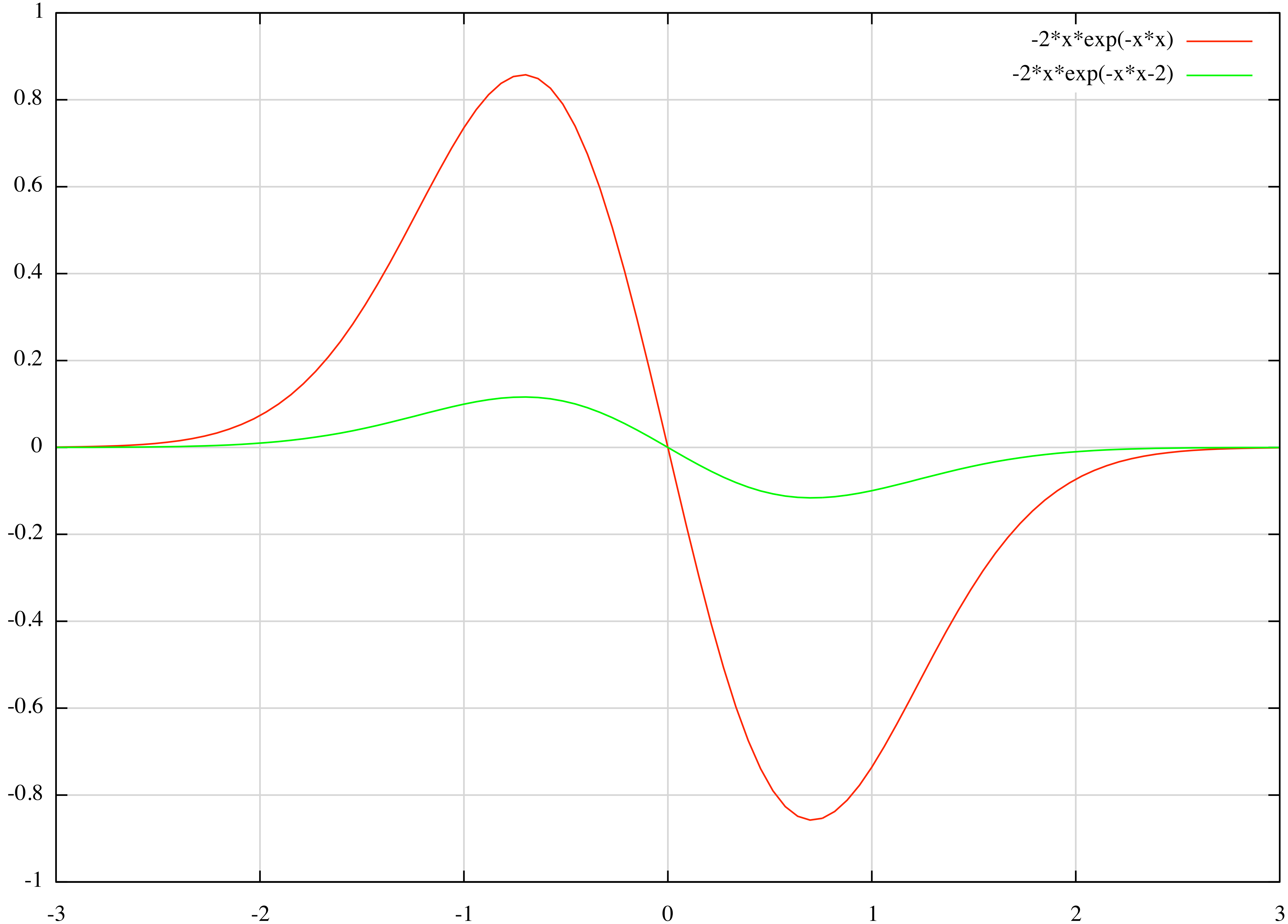
家のPC，MACでも使用可。

式をいれたコマンドを叩くだけ

```
gnuplot> plot -2*x*exp(-x*x), -2*x*exp(-x*x-2)
gnuplot> set grid
gnuplot> set xrange [-3:3]
gnuplot> replot
```

詳しい使い方は「gnuplot tips」で検索を

http://folk.uio.no/hpl/scripting/doc/gnuplot/Kawano/


-2*x*exp(-x*x)
-2*x*exp(-x*x-2)
1
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1
-3
-2
-1
0
1
2
3

３次元プロットもできる

```
gnuplot> splot exp(-x*x-2*y*y)
gnuplot> set hidden3d
gnuplot> set isosample 40
gnuplot> set xrange [-3:3]
gnuplot> set yrange [-3:3]
gnuplot> set contour
        gnuplot> set cntrparam level 10
gnuplot> replot
```

３次元プロットもできる

gnuplot> splot exp(-x*x-2*y*y)

gnuplot> set hidden3d

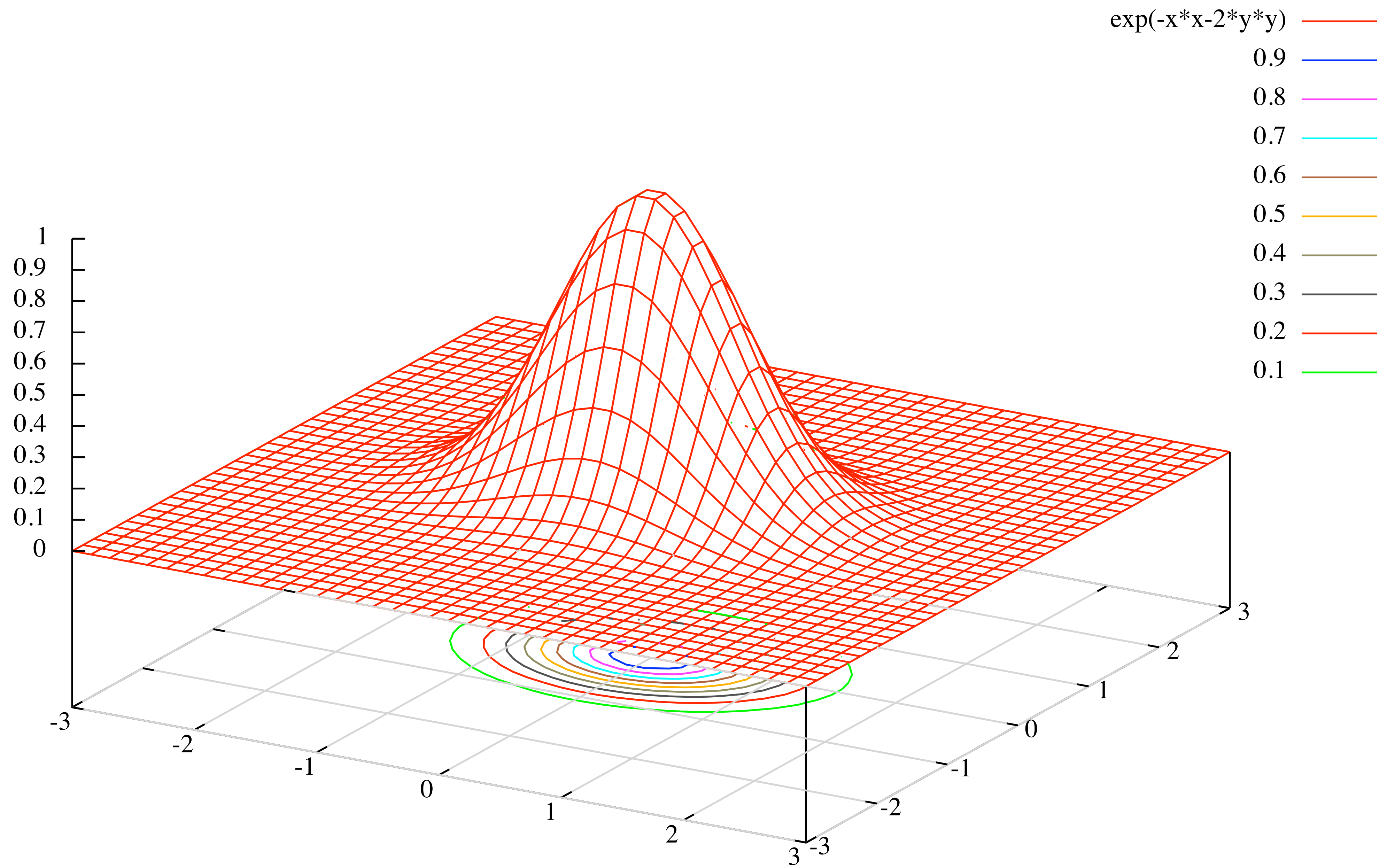
gnuplot> set isosample 40

gn

gn

gn

gn

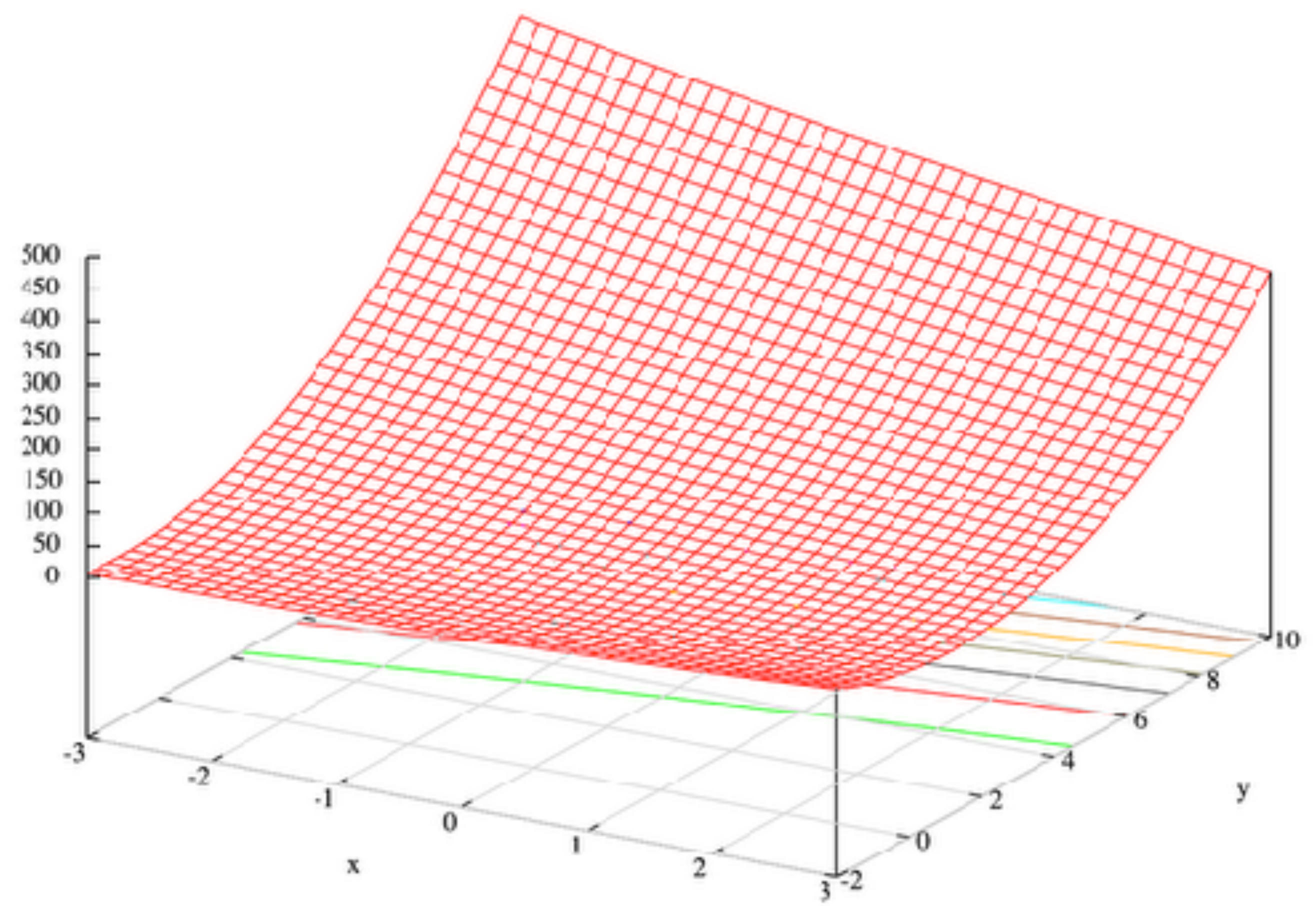


演習 I

$$f(x, y) = x^2 - 3xy + 4y^2$$

$$\frac{\partial f}{\partial x} = ?$$

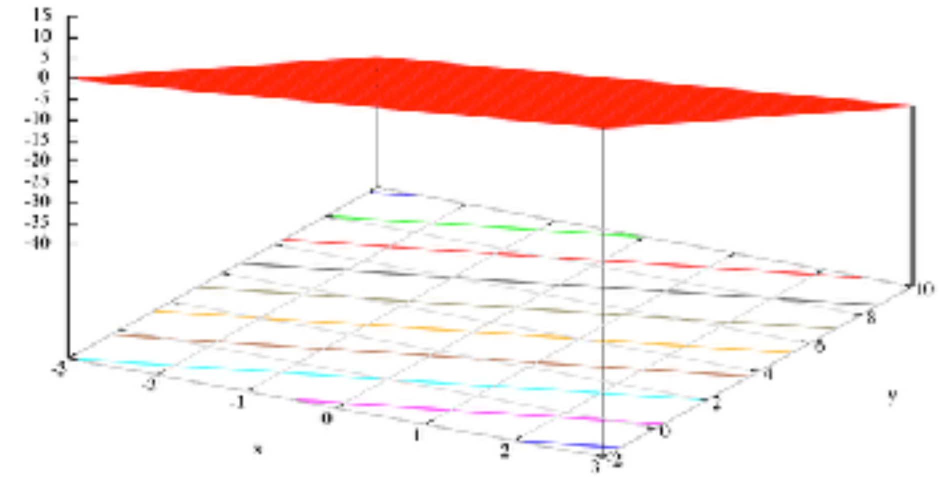
$$\frac{\partial f}{\partial y} = ?$$



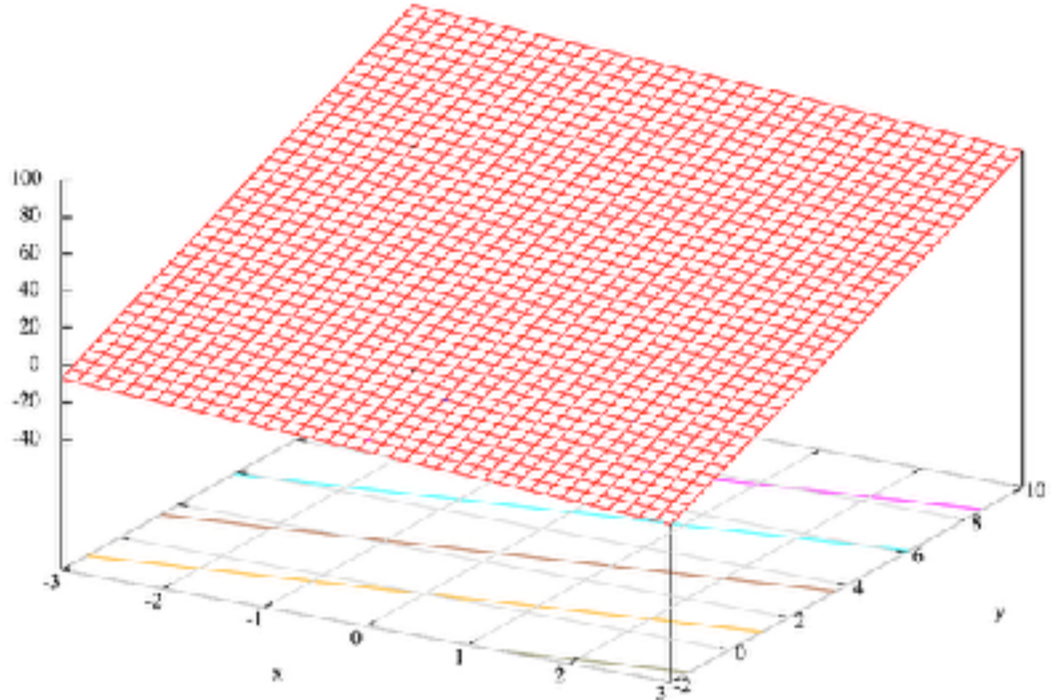
解答I

$$f(x,y) = x^2 - 3xy + 4y^2$$

$$\frac{\partial f}{\partial x} = 2x - 3y$$



$$\frac{\partial f}{\partial y} = -3x + 8y$$

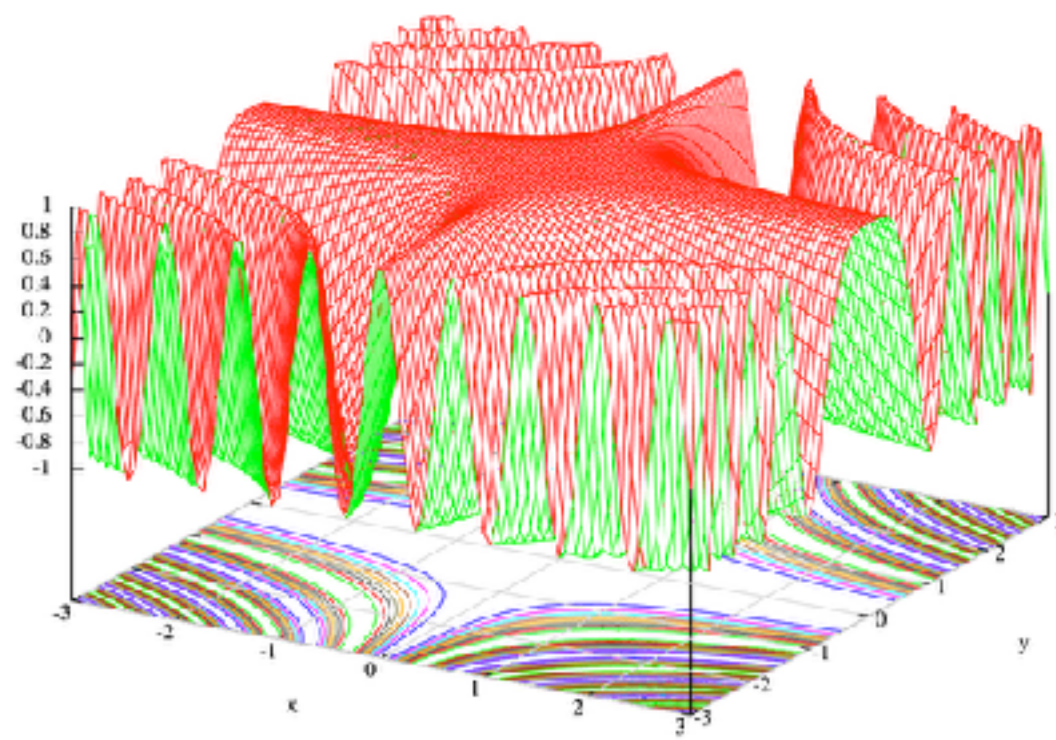


演習 II

$$f(x,y) = \cos(xy^2)$$

$$\frac{\partial f}{\partial x} = ?$$

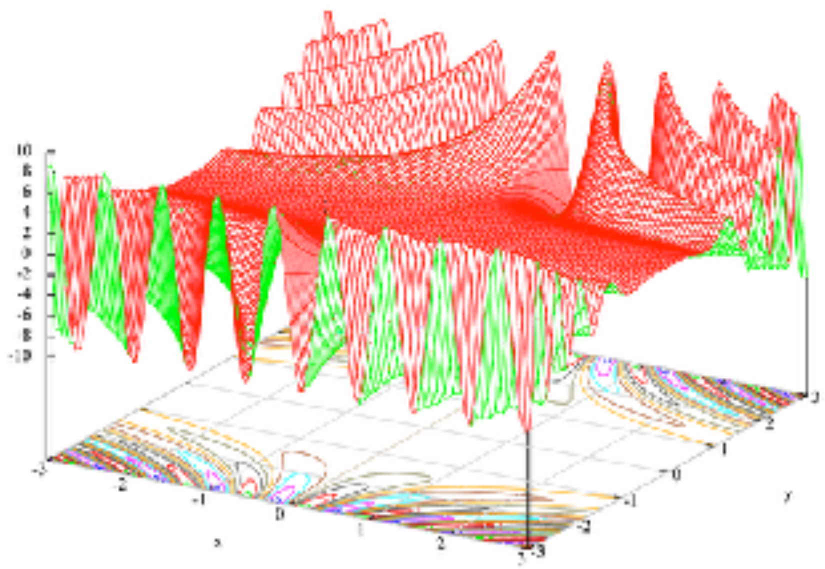
$$\frac{\partial f}{\partial y} = ?$$



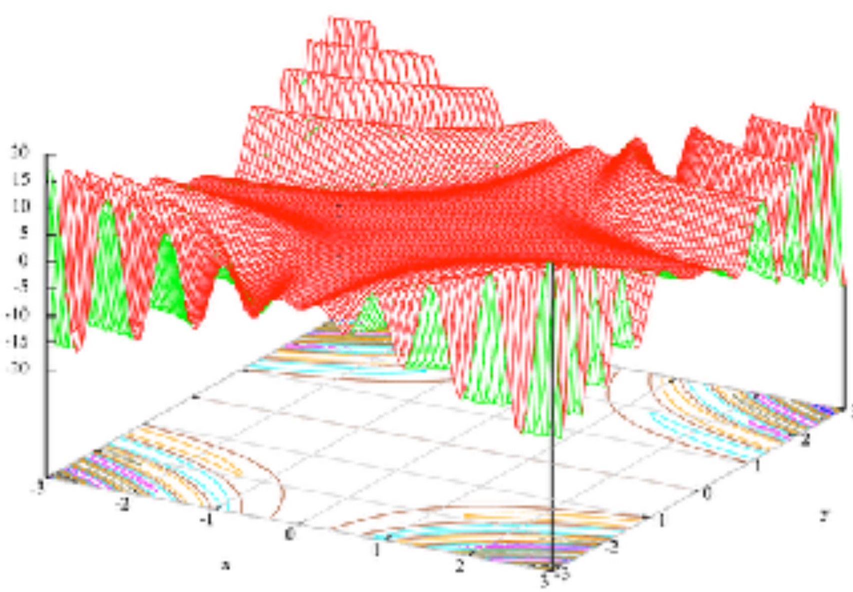
解答II

$$f(x, y) = \cos(xy^2)$$

$$\frac{\partial f}{\partial x} = -\sin(xy^2)y^2$$



$$\frac{\partial f}{\partial y} = -\sin(xy^2)2xy$$



演習 III

$$f(x, y) = (2x + 3y)\ln(x^2 + y^2)$$

$$\frac{\partial f}{\partial x} = ?$$

$$\frac{\partial f}{\partial y} = ?$$

解答III

$$f(x,y) = (2x+3y)\ln(x^2+y^2)$$

$$\frac{\partial f}{\partial x} = 2\ln(x^2+y^2) + (2x+3y)\frac{1}{x^2+y^2}2x$$

$$\frac{\partial f}{\partial y} = 3\ln(x^2+y^2) + (2x+3y)\frac{1}{x^2+y^2}2y$$

演習 IV

$$f(x,y) = \frac{x-y}{x+y}$$

$$\frac{\partial f}{\partial x} = ?$$

$$\frac{\partial f}{\partial y} = ?$$

解答IV

$$f(x,y) = \frac{x-y}{x+y}$$

$$\frac{\partial f}{\partial x} = \frac{1}{x+y} - \frac{x-y}{(x+y)^2} = \frac{2y}{(x+y)^2}$$

$$\frac{\partial f}{\partial y} = \frac{-1}{x+y} - \frac{x-y}{(x+y)^2} = -\frac{2x}{(x+y)^2}$$

２階偏微分

$$\frac{\partial}{\partial x}\frac{\partial f}{\partial x} = \frac{\partial^2 f}{\partial x^2}$$

$$\frac{\partial}{\partial y}\frac{\partial f}{\partial y} = \frac{\partial^2 f}{\partial y^2}$$

交差微分 $$\frac{\partial}{\partial y}\frac{\partial f}{\partial x} = \frac{\partial^2 f}{\partial y \partial x}$$ ：xを先にyが後

交差微分 $$\frac{\partial}{\partial x}\frac{\partial f}{\partial y} = \frac{\partial^2 f}{\partial x \partial y}$$ ：yを先にxが後

演習V

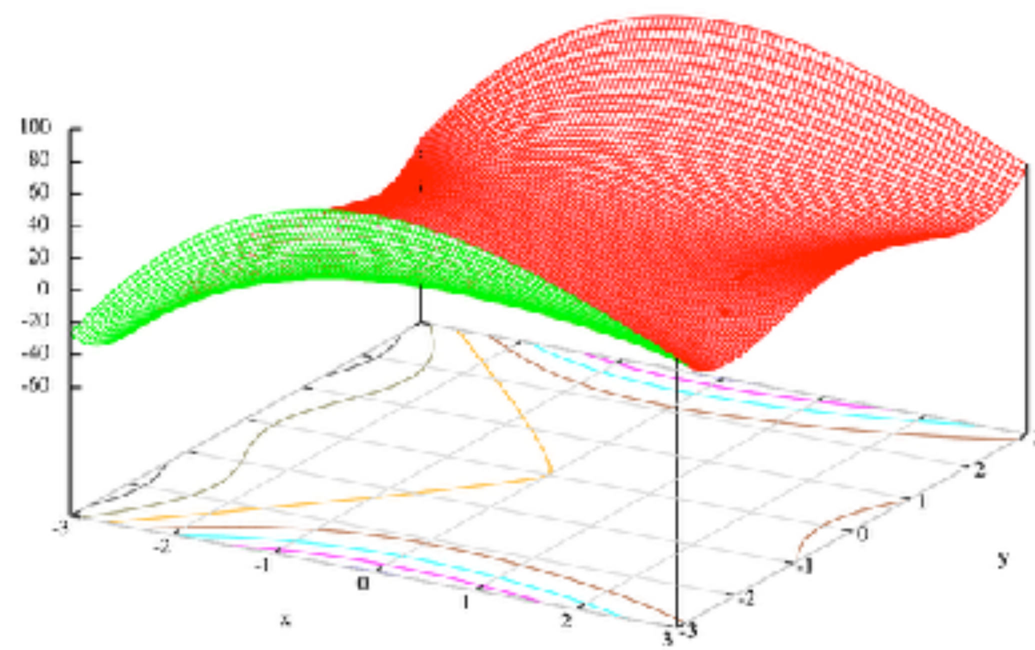
$$f(x,y) = x^3 - x^2y^2 + y^4$$

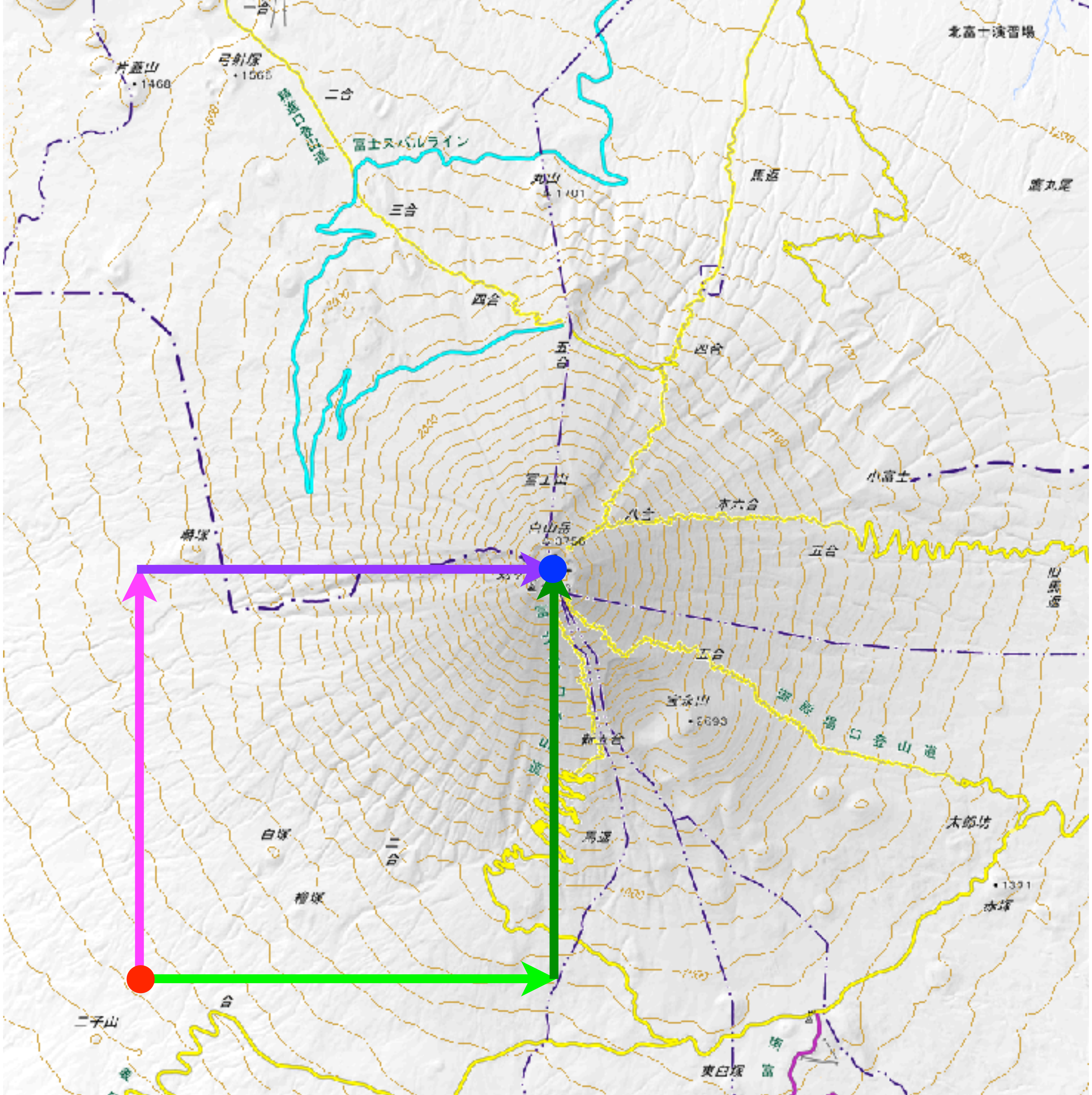
$$\frac{\partial}{\partial x}\frac{\partial f}{\partial x} = \frac{\partial^2 f}{\partial x^2} = ?$$

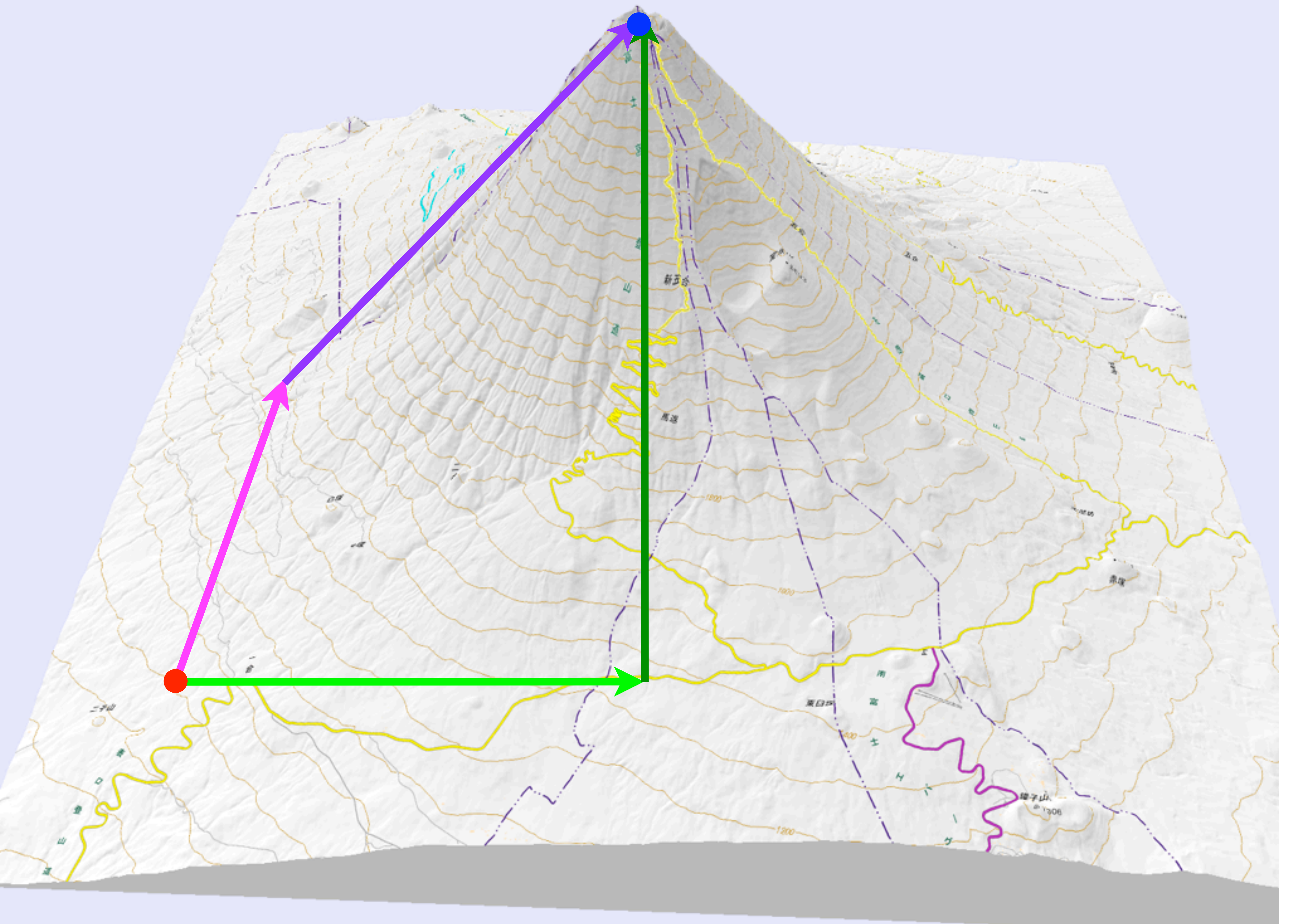
$$\frac{\partial}{\partial y}\frac{\partial f}{\partial y} = \frac{\partial^2 f}{\partial y^2} = ?$$

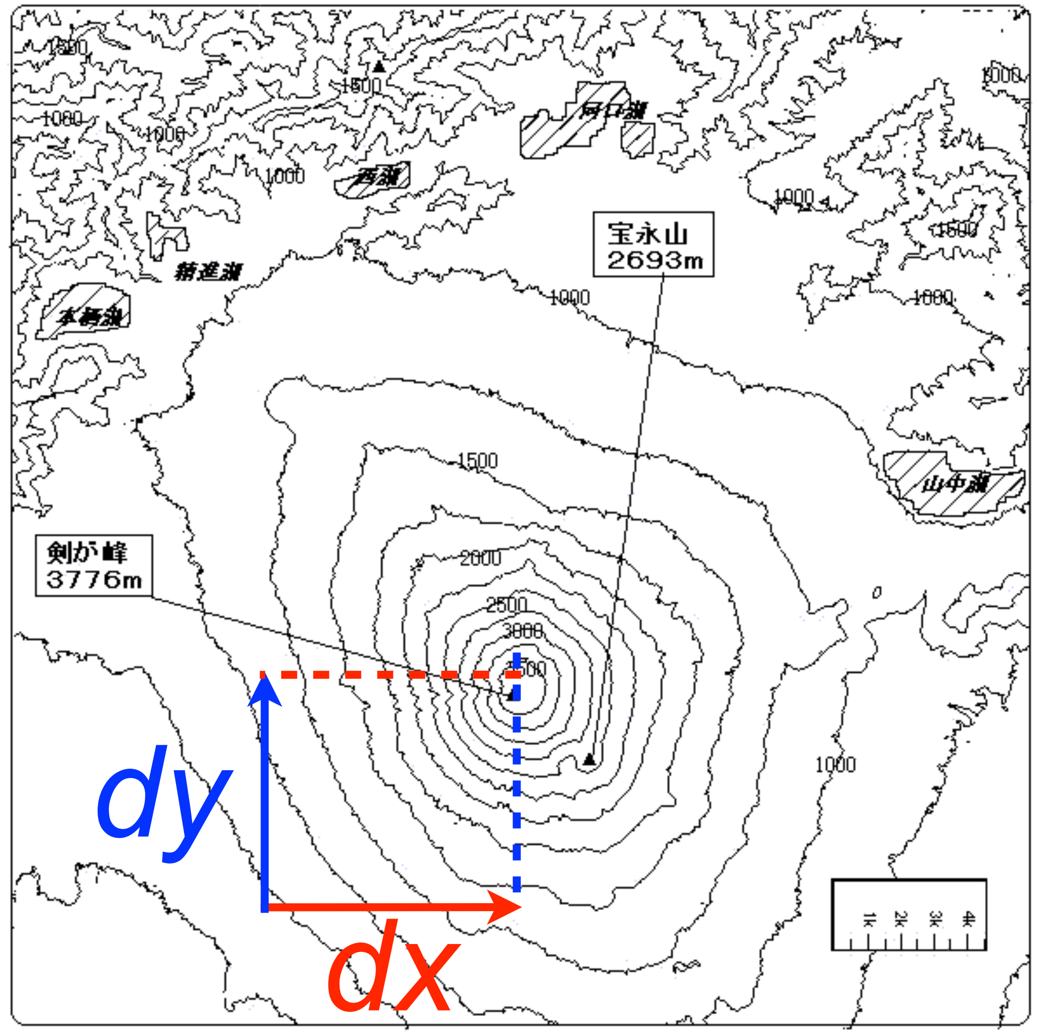
$$\frac{\partial}{\partial y}\frac{\partial f}{\partial x} = \frac{\partial^2 f}{\partial y \partial x} = ?$$

$$\frac{\partial}{\partial x}\frac{\partial f}{\partial y} = \frac{\partial^2 f}{\partial x \partial y} = ?$$




北富士演習場
片蓋山
弓射塚
二合
富士スバルライン
馬返
鷹丸尾
三合
四合
五合
富士山
小富士
白山岳
宝永山
太郎坊
二子山
東臼塚



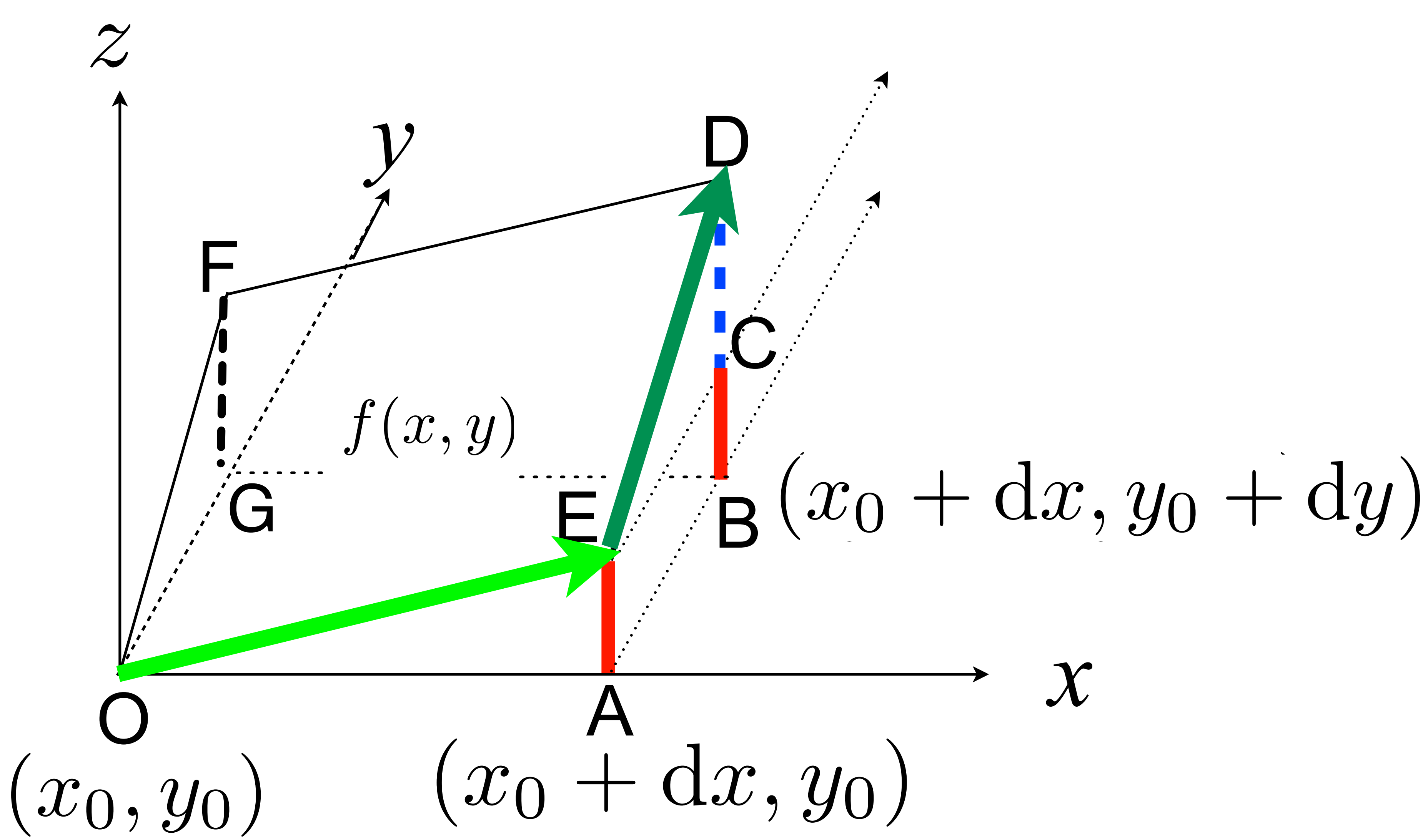


$$df = f(x_0 + dx, y_0 + dy) - f(x_0, y_0)$$

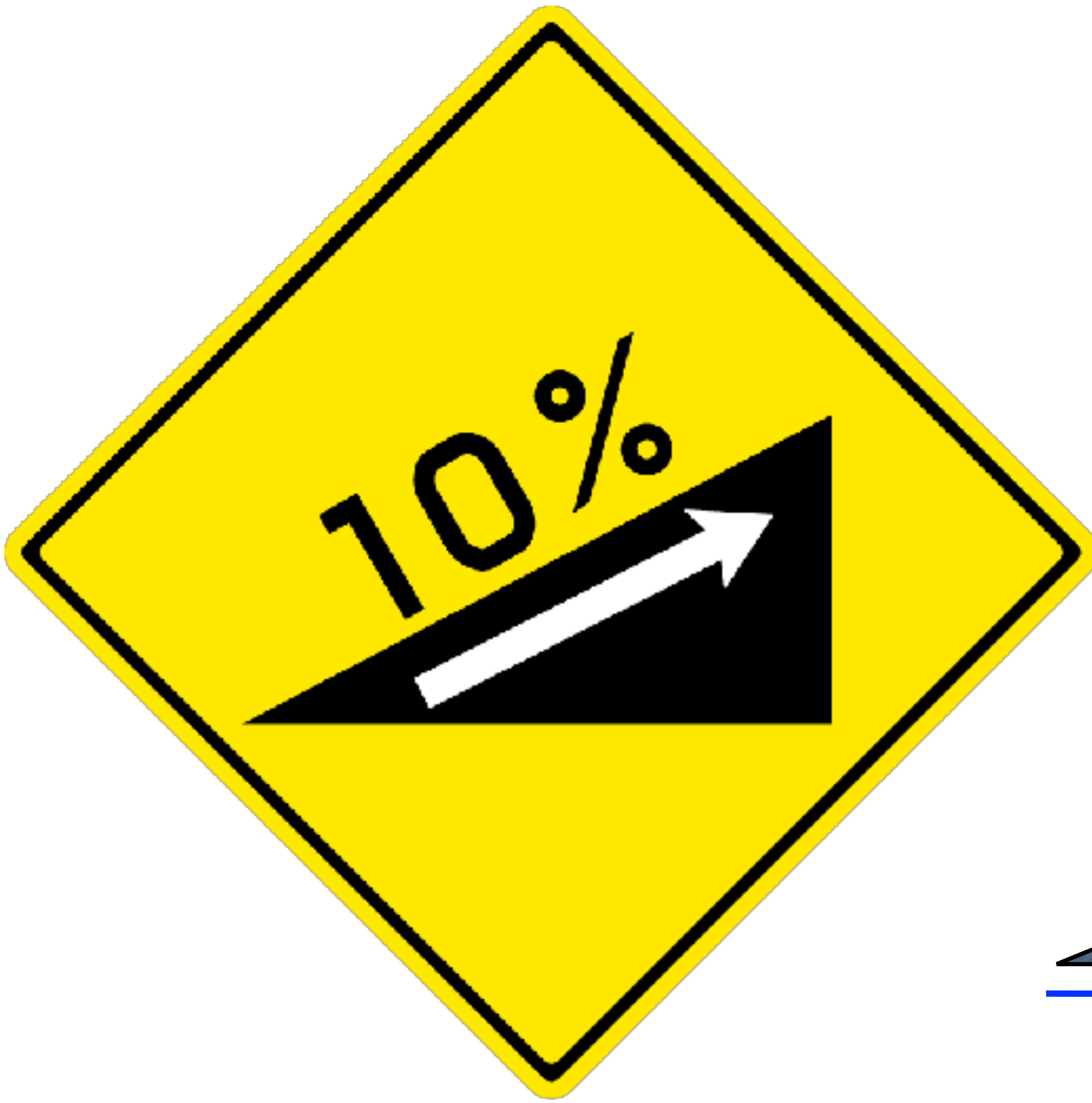
はどのように表されるのか？

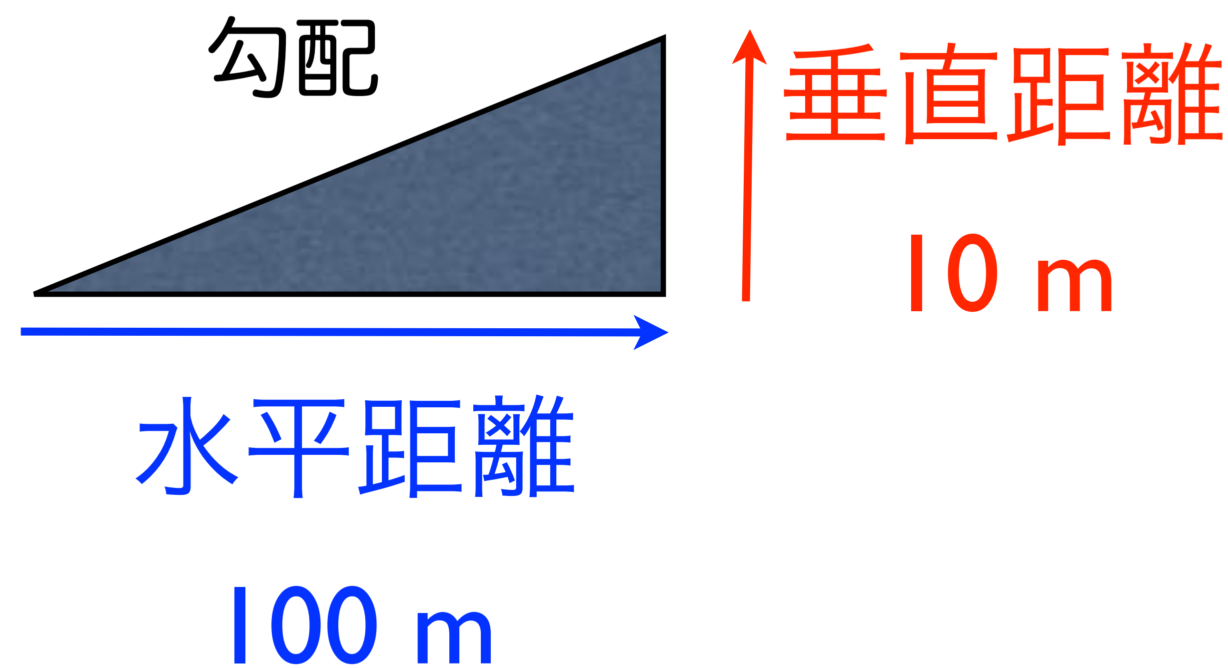
その１(緑ルート）

$$
\begin{aligned}
\mathrm{d}f &= f(x_0+\mathrm{d}x, y_0+\mathrm{d}y) - f(x_0, y_0) \\
&= [f(x_0+\mathrm{d}x, y_0+\mathrm{d}y) - f(x_0+\mathrm{d}x, y_0)] + [f(x_0+\mathrm{d}x, y_0) - f(x_0, y_0)]
\end{aligned}
$$

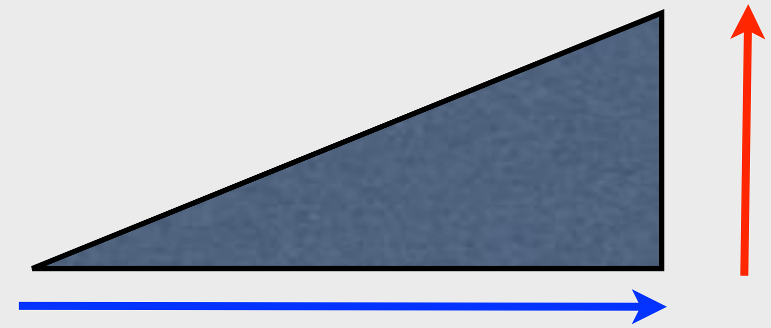


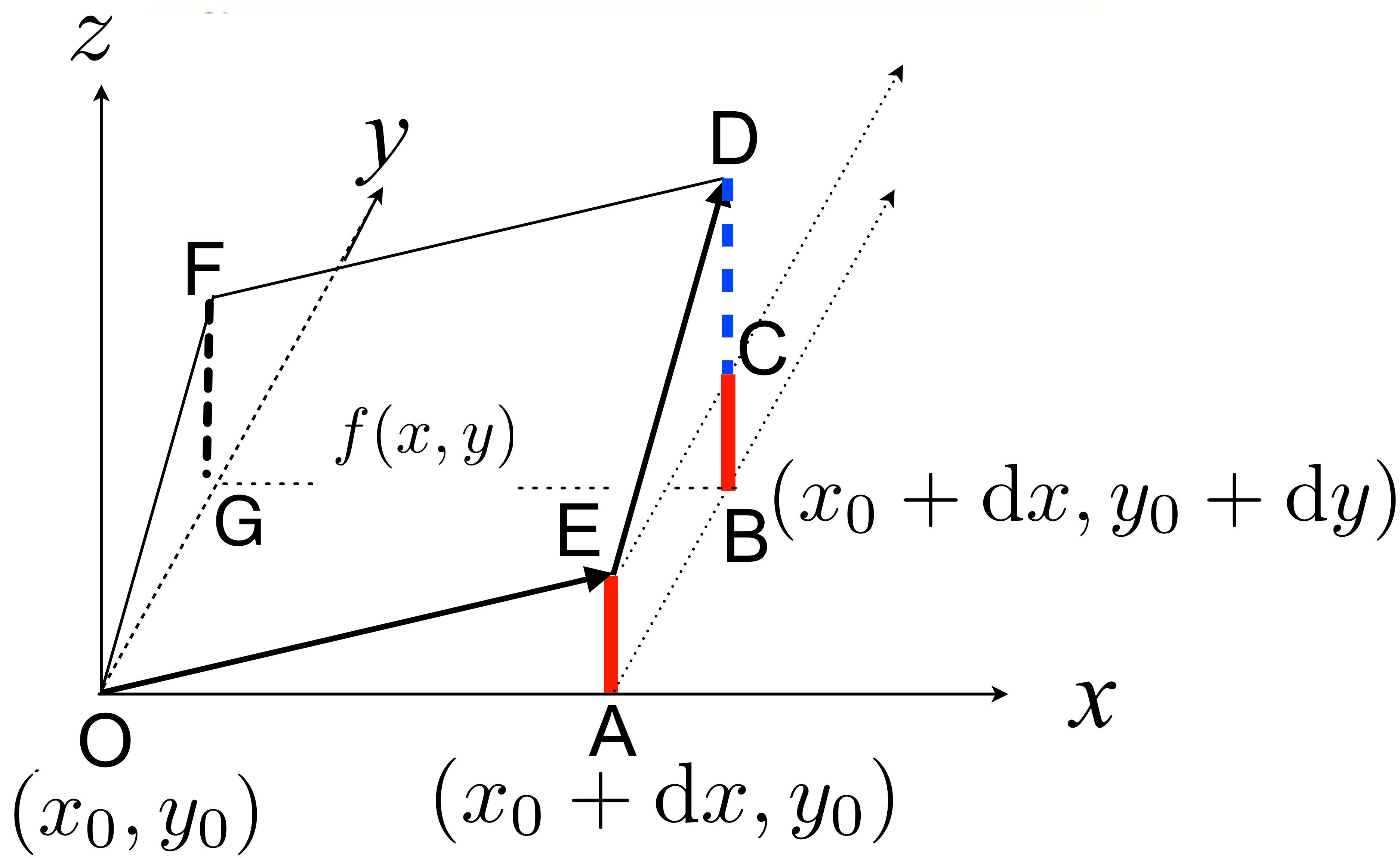
道路勾配［%］ ＝ １００ x 垂直距離［m］／水平距離［m］





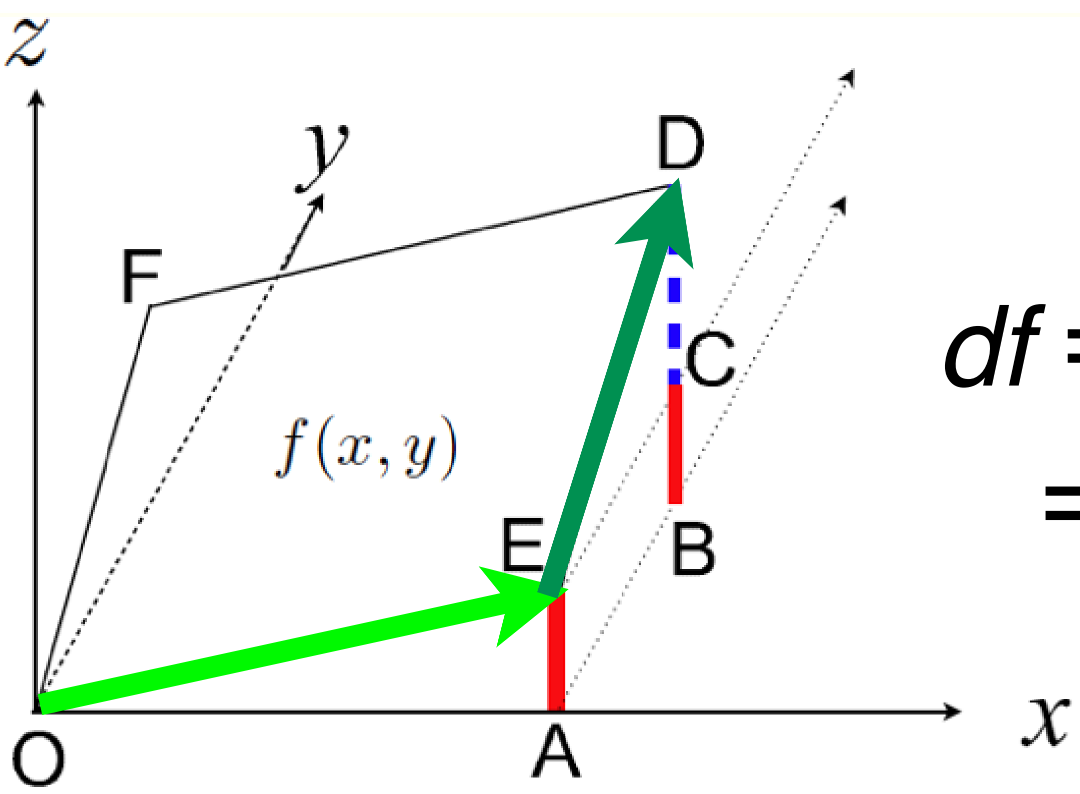
高さ = 勾配×距離





$$df = |BD| = |BC| + |CD| = |AE| + |CD|$$

$$= \mathrm{slope}(\overrightarrow{OE})|OA| + \mathrm{slope}(\overrightarrow{ED})|EC|$$



df = |BD| = |BC| + |CD| = |AE| + |CD|

= slope($\overrightarrow{OE}$)|OA| + slope($\overrightarrow{ED}$)|EC|

$$g(x+dx) \simeq g(x) + g'dx$$

$$\begin{aligned}
\mathrm{d}f &= \left(\frac{\partial f}{\partial x}\right)_{y_0} \mathrm{d}x + \left(\frac{\partial f}{\partial y}\right)_{x_0+\mathrm{d}x} \mathrm{d}y \\
&\simeq \left(\frac{\partial f}{\partial x}\right)_{y_0} \mathrm{d}x + \left\{ \left(\frac{\partial f}{\partial y}\right)_{x_0} + \left[\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)_{x_0}\right]_{y_0} \mathrm{d}x \right\} \mathrm{d}y \\
&= \left(\frac{\partial f}{\partial x}\right)_{y_0} \mathrm{d}x + \left(\frac{\partial f}{\partial y}\right)_{x_0} \mathrm{d}y + \left[\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)_{x_0}\right]_{y_0} \mathrm{d}x\mathrm{d}y \\
&= \left(\frac{\partial f}{\partial x}\right)_{y_0} \mathrm{d}x + \left(\frac{\partial f}{\partial y}\right)_{x_0} \mathrm{d}y + \left(\frac{\partial f_y}{\partial x}\right)_{y_0} \mathrm{d}x\mathrm{d}y
\end{aligned}$$

$$g'(x) = \frac{dg(x)}{dx} = \lim_{dx \to 0} \frac{g(x + dx) - g(x)}{dx}$$

$$g'(x)dx \simeq g(x + dx) - g(x)$$

$$g(x + dx) \simeq g(x) + g'(x)dx$$

$$g'(x) = \lim_{\mathrm{d}x \to 0} \frac{g(x + \mathrm{d}x) - g(x)}{\mathrm{d}x} \;\mapsto\; g(x + \mathrm{d}x) \simeq g(x) + g'(x)\mathrm{d}x$$

$$\left(\frac{\partial f}{\partial y}\right)_{x_0 + \mathrm{d}x} \;\mapsto\; g(x_0 + \mathrm{d}x)$$

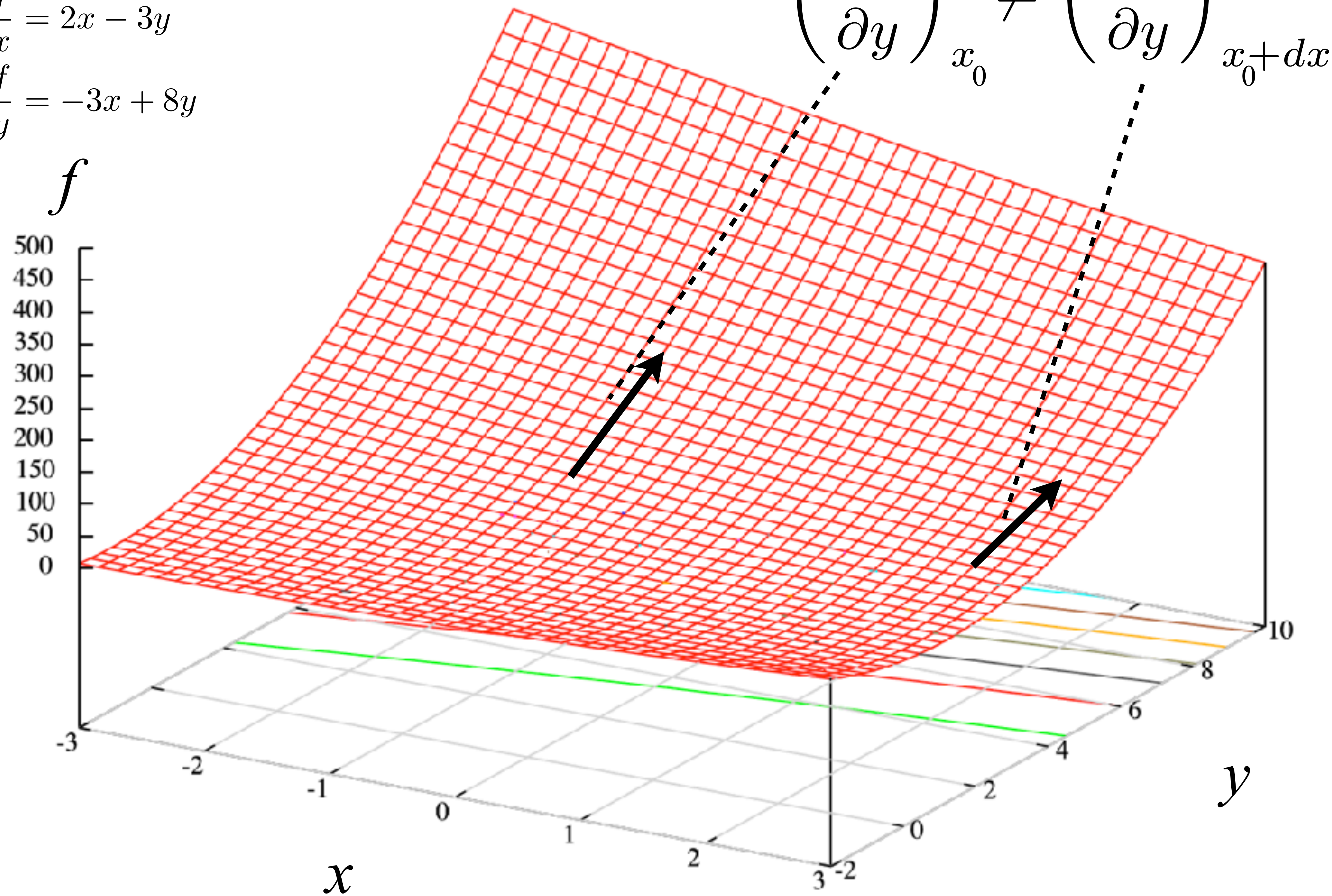
$$\underbrace{\left(\frac{\partial f}{\partial y}\right)_{x_0 + \mathrm{d}x}}_{=\ g(x_0 + \mathrm{d}x)} \simeq \underbrace{\left(\frac{\partial f}{\partial y}\right)_{x_0}}_{=\ g(x_0)} + \underbrace{\left[\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)_{x_0}\right]_{y_0}}_{=\ g'(x_0)} \mathrm{d}x$$

$$f(x,y) = x^2 - 3xy + 4y^2$$

$$\frac{\partial f}{\partial x} = 2x - 3y$$

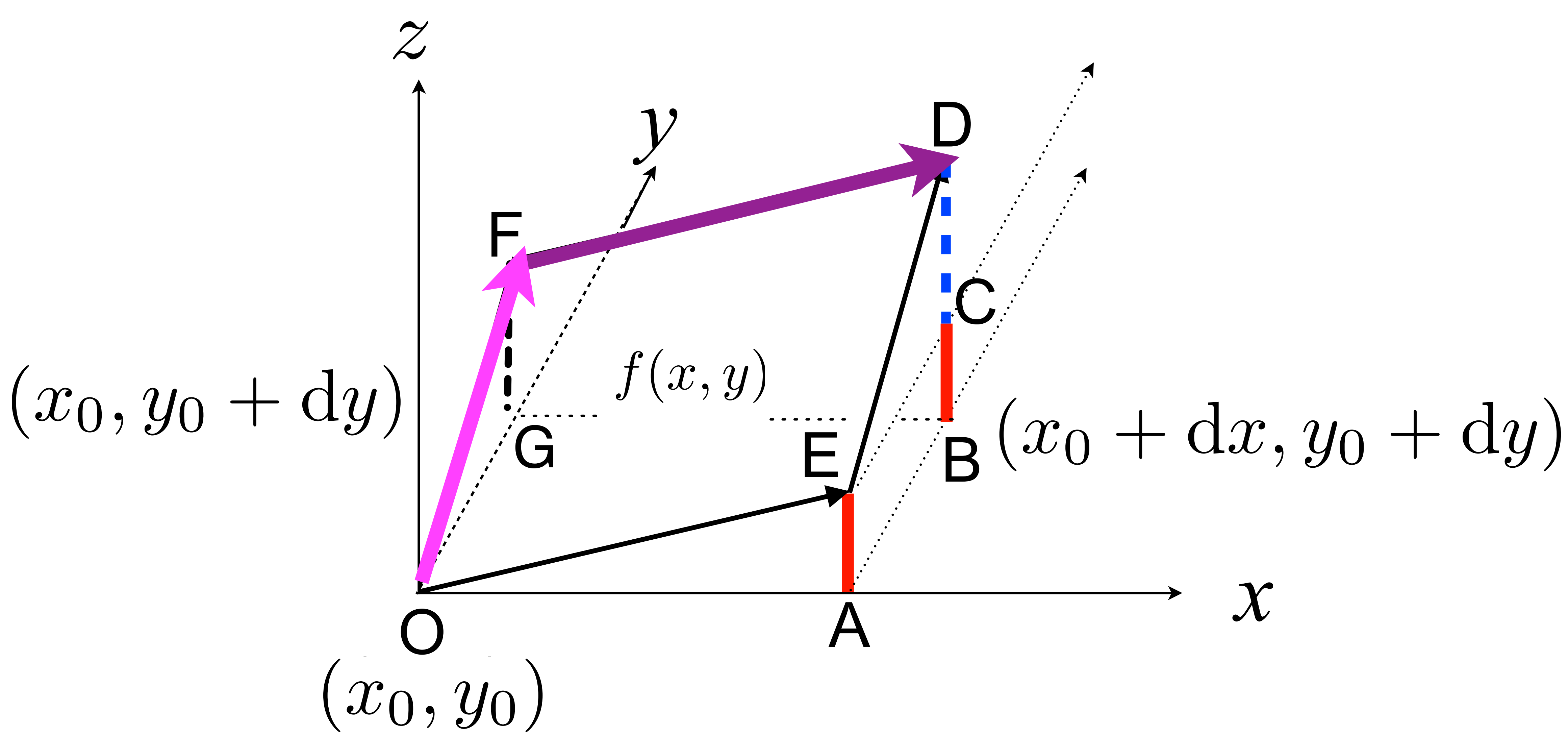
$$\frac{\partial f}{\partial y} = -3x + 8y$$

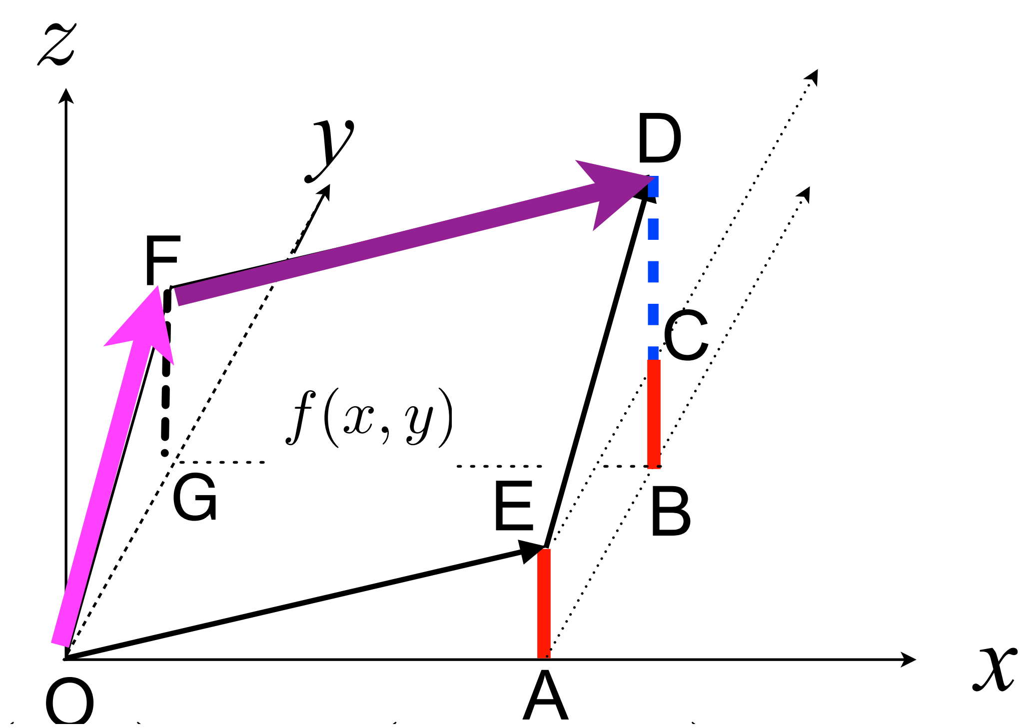
$$\left(\frac{\partial f}{\partial y}\right)_{x_0} \neq \left(\frac{\partial f}{\partial y}\right)_{x_0 + dx}$$



その２(ピンクルート）

$$
\begin{aligned}
\mathrm{d}f &= f(x_0+\mathrm{d}x, y_0+\mathrm{d}y) - f(x_0, y_0) \\
&= [f(x_0+\mathrm{d}x, y_0+\mathrm{d}y) - f(x_0, y_0+\mathrm{d}y)] + [f(x_0, y_0+\mathrm{d}y) - f(x_0, y_0)]
\end{aligned}
$$





df
= slope(OF)|AB| + slope(FD)|OA|

$$h(y+dy) \simeq h(y) + h'(y)dy$$

$$\mathrm{d}f = \left(\frac{\partial f}{\partial y}\right)_{x_0} \mathrm{d}y + \left(\frac{\partial f}{\partial x}\right)_{y_0+\mathrm{d}y} \mathrm{d}x$$

$$\simeq \left(\frac{\partial f}{\partial y}\right)_{x_0} \mathrm{d}y + \left\{\left(\frac{\partial f}{\partial x}\right)_{y_0} + \left[\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)_{y_0}\right]_{x_0} \mathrm{d}y\right\} \mathrm{d}x$$

$$= \left(\frac{\partial f}{\partial x}\right)_{y_0} \mathrm{d}x + \left(\frac{\partial f}{\partial y}\right)_{x_0} \mathrm{d}y + \left[\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)_{y_0}\right]_{x_0} \mathrm{d}x\mathrm{d}y$$

$$= \left(\frac{\partial f}{\partial x}\right)_{y_0} \mathrm{d}x + \left(\frac{\partial f}{\partial y}\right)_{x_0} \mathrm{d}y + \left(\frac{\partial f_x}{\partial y}\right)_{x_0} \mathrm{d}x\mathrm{d}y$$

$$h'(y) = \frac{dh(y)}{dy} = \lim_{dy \to 0} \frac{h(y + dy) - h(y)}{dy}$$

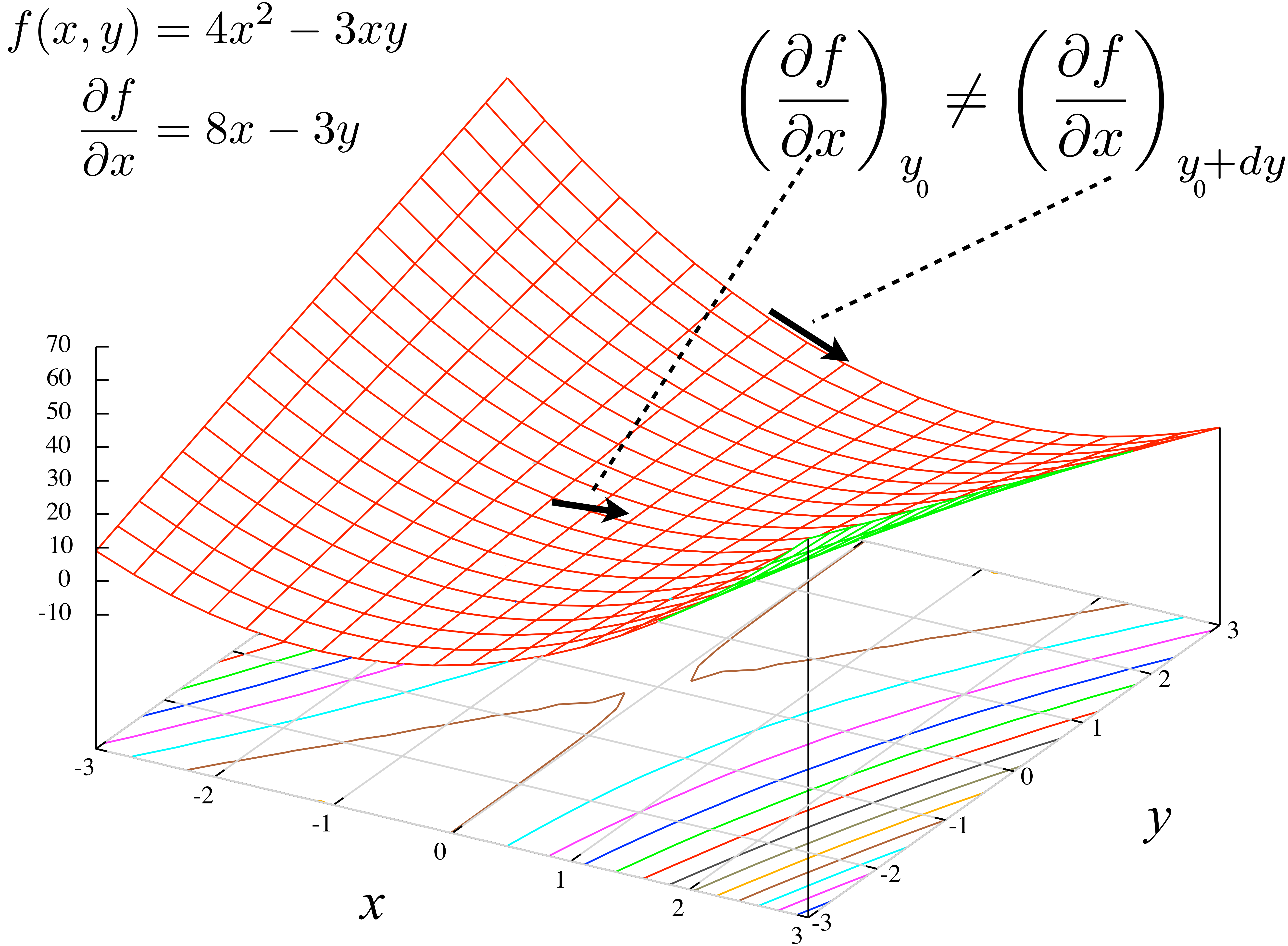
$$h'(x)dy \simeq h(y + dy) - h(y)$$

$$h(y + dy) \simeq h(y) + h'(y)dy$$

$$h'(y) = \lim_{\mathrm{d}y \to 0} \frac{h(y + \mathrm{d}y) - h(y)}{\mathrm{d}y} \;\mapsto\; h(y + \mathrm{d}y) \simeq h(y) + h'(y)\mathrm{d}y$$

$$\left(\frac{\partial f}{\partial x}\right)_{y_0 + \mathrm{d}y} \;\mapsto\; h(y_0 + \mathrm{d}y)$$

$$\underbrace{\left(\frac{\partial f}{\partial x}\right)_{y_0 + \mathrm{d}y}}_{= \, h(y_0 + \mathrm{d}y)} \simeq \underbrace{\left(\frac{\partial f}{\partial x}\right)_{y_0}}_{= \, h(y_0)} + \underbrace{\left[\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)_{y_0}\right]_{x_0}}_{= \, h'(y_0)} \mathrm{d}y$$


$f(x,y) = 4x^2 - 3xy$
$\frac{\partial f}{\partial x} = 8x - 3y$
$\left(\frac{\partial f}{\partial x}\right)_{y_0} \neq \left(\frac{\partial f}{\partial x}\right)_{y_0+dy}$
70
60
50
40
30
20
10
0
-10
-3
-2
-1
0
1
2
3
x
-3
-2
-1
0
1
2
3
y

同じ $df(x,y)$ を与えるには，２つの交差微分が等しい

どこの x, y でも成立するために，x_0,y_0 の0をはずして

$$\left(\frac{\partial f_x}{\partial y}\right)_x = \left(\frac{\partial f_y}{\partial x}\right)_y$$

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

完全微分という

内部圧　$\pi_T = \left(\frac{\partial U}{\partial V}\right)_T$

（理想気体では）ゼロであることを実験で示した。数式で示そう。

Uは，$U(S,V)$の関数として（第一法則）

$$dU = TdS - PdV = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

$S = S(V,T)$としてTを一定に保ったまま両辺をdVで割ると

$$\begin{aligned} \pi_T &= \left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\partial U}{\partial S}\right)_V \left(\frac{\partial S}{\partial V}\right)_T + \left(\frac{\partial U}{\partial V}\right)_S \underbrace{\left(\frac{\partial V}{\partial V}\right)_T}_{=1} \\ &= T\left(\frac{\partial S}{\partial V}\right)_T - P \end{aligned}$$

$$u = u(x, y)$$

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

$$y = y(x, z)$$

zを一定にして，dxで割る

$$\left(\frac{\partial u}{\partial x}\right)_z = \left(\frac{\partial u}{\partial x}\right)_y \underbrace{\left(\frac{\partial x}{\partial x}\right)_z}_{=1} + \left(\frac{\partial u}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z$$

$$= \left(\frac{\partial u}{\partial x}\right)_y + \left(\frac{\partial u}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z$$

$$
\begin{aligned}
dA &= -SdT - PdV \\
-\left(\frac{\partial S}{\partial V}\right)_T &= -\left(\frac{\partial P}{\partial T}\right)_V
\end{aligned}
$$

Maxwellの関係式

内部圧

$$\pi_T = \left(\frac{\partial U}{\partial V}\right)_T$$

$$
\begin{aligned}
\pi_T &= T\left(\frac{\partial S}{\partial V}\right)_T - P \\
&= T\left(\frac{\partial P}{\partial T}\right)_V - P
\end{aligned}
$$

理想気体の時

$$
\begin{aligned}
PV &= nRT \\
\pi_T &= T\frac{nR}{V} - P = 0
\end{aligned}
$$

別解マッカリー 化学数学（藤森，松澤，筑紫訳 丸善）より

$$\pi_T = \left(\frac{\partial U}{\partial V}\right)_T$$

について求めたいので，内部エネルギーUを体積Vと温度Tの関数$U(V, T)$だとする。

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT \qquad \textbf{(*)}$$

同じくエントロピーSを体積Vと温度Tの関数とする

$$dS = \left(\frac{\partial S}{\partial V}\right)_T dV + \left(\frac{\partial S}{\partial T}\right)_V dT$$

第一法則より$\mathrm{d}U$は

$$dU = TdS - PdV$$

これに$\mathrm{d}S$を代入して

$$= \underbrace{\left[T\left(\frac{\partial S}{\partial V}\right)_T - P\right]}_{=\left(\frac{\partial U}{\partial V}\right)_T} dV + \underbrace{T\left(\frac{\partial S}{\partial T}\right)_V}_{=\left(\frac{\partial U}{\partial T}\right)_V} dT$$

$$dA = -SdT - PdV, \quad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$ より

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

$$T\left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial Q}{\partial T}\right)_V = C_V$$

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T}$$

理想気体における$\left(\frac{\partial H}{\partial P}\right)_T$を求めたい

エンタルピーHを圧力Pと温度Tの関数$H(P, T)$だとする。

$$dH = \left(\frac{\partial H}{\partial P}\right)_T dP + \left(\frac{\partial H}{\partial T}\right)_P dT$$

エントロピーSを圧力Pと温度Tの関数とする。

$$dS = \left(\frac{\partial S}{\partial P}\right)_T dP + \left(\frac{\partial S}{\partial T}\right)_P dT$$

$$dH = TdS + VdP$$

これにdSを代入して

$$dH = \underbrace{\left[T\left(\frac{\partial S}{\partial P}\right)_T + V\right]}_{=\left(\frac{\partial H}{\partial P}\right)_T} dP + \underbrace{T\left(\frac{\partial S}{\partial T}\right)_P}_{=\left(\frac{\partial H}{\partial T}\right)_P} dT$$

$$dG = V\,dP - S\,dT, \quad \left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$$

$$\begin{aligned}\left(\frac{\partial H}{\partial P}\right)_T &= -T\left(\frac{\partial V}{\partial T}\right)_P + V \\ &= -T\frac{nR}{P} + V = -V + V = 0, \quad \text{(ideal gas)}\end{aligned}$$

$$\begin{aligned}T\left(\frac{\partial S}{\partial T}\right)_P &= \left(\frac{\partial H}{\partial T}\right)_P = C_P \\ \left(\frac{\partial S}{\partial T}\right)_P &= \frac{C_P}{T}\end{aligned}$$

さらにややこしい関係式を導く

エントロピーSを体積Vと温度Tの関数とする

$$dS = \underbrace{\left(\frac{\partial S}{\partial V}\right)_T}_{=\left(\frac{\partial P}{\partial T}\right)_V} dV + \underbrace{\left(\frac{\partial S}{\partial T}\right)_V}_{=\frac{C_V}{T}} dT$$

体積Vを温度TとPの関数とする

$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP$$

$$\begin{aligned} dS &= \left(\frac{\partial P}{\partial T}\right)_V \left[\left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP\right] + \frac{C_V}{T} dT \\ &= \left[\frac{C_V}{T} + \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P\right] dT + \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial P}\right)_T dP \end{aligned}$$

$$dS = \left[\frac{C_V}{T} + \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P\right] dT + \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial P}\right)_T dP$$

$$dS = \underbrace{\left(\frac{\partial S}{\partial T}\right)_P}_{=\frac{C_P}{T}} dT + \underbrace{\left(\frac{\partial S}{\partial P}\right)_T}_{=-\left(\frac{\partial V}{\partial T}\right)_P} dP$$

$$C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P$$

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

$$\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T = -1$$

理想気体にあてはめると

$$C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P$$
$$= T\frac{nR}{V}\frac{nR}{P} = T\frac{(nR)^2}{nRT} = nR$$

$$\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T = \frac{nR}{V}\frac{P}{nR}\frac{-nRT}{P^2} = -\frac{nRT}{PV} = -1$$

状態関数
と
完全微分

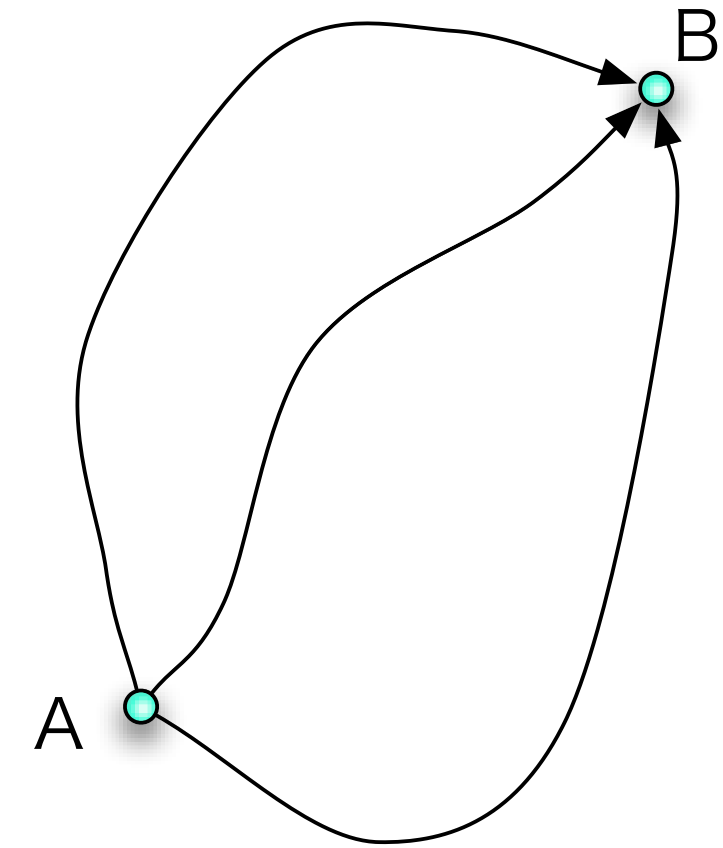
状態関数：経路によらず２つの状態間の差で決まる。

例：内部エネルギー

経路による場合

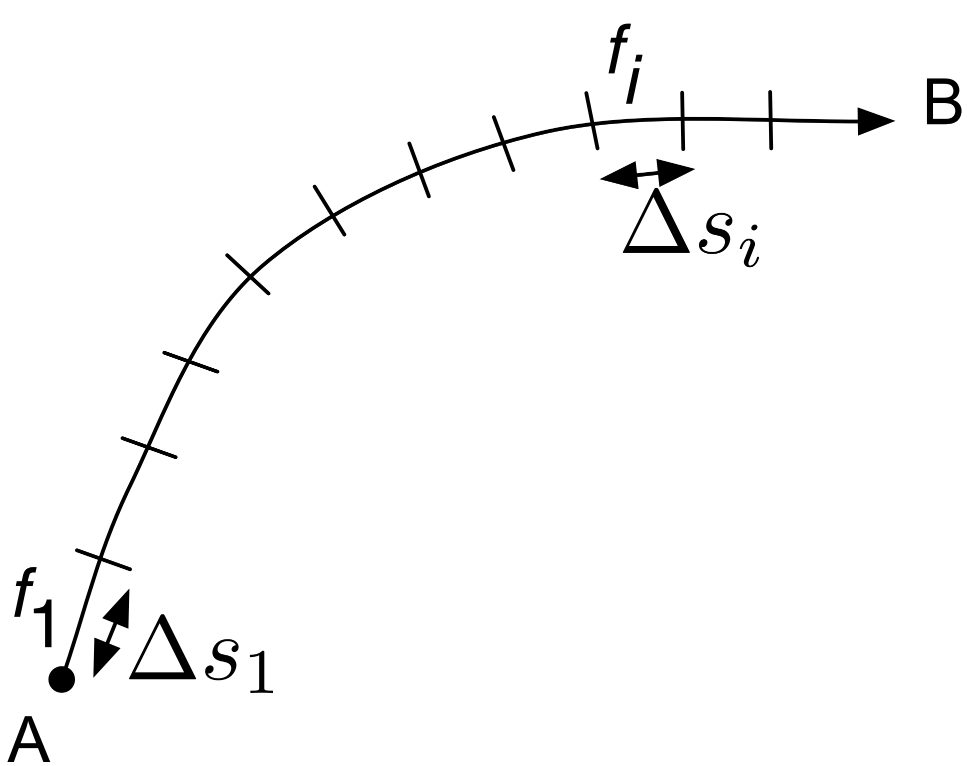
例：熱，　仕事

線積分 line integral



$$\int_C f(x,y)ds = \lim_{\Delta s_i \to 0} \sum_i f_i \Delta s_i$$

$$f_i = f(x_i, y_i)$$



曲線を微小な弧に分割して,
それぞれの長さを, $\Delta s_1, \Delta s_2, ... \Delta s_i, ...$
とする。

ここは高度なのでskipしていい

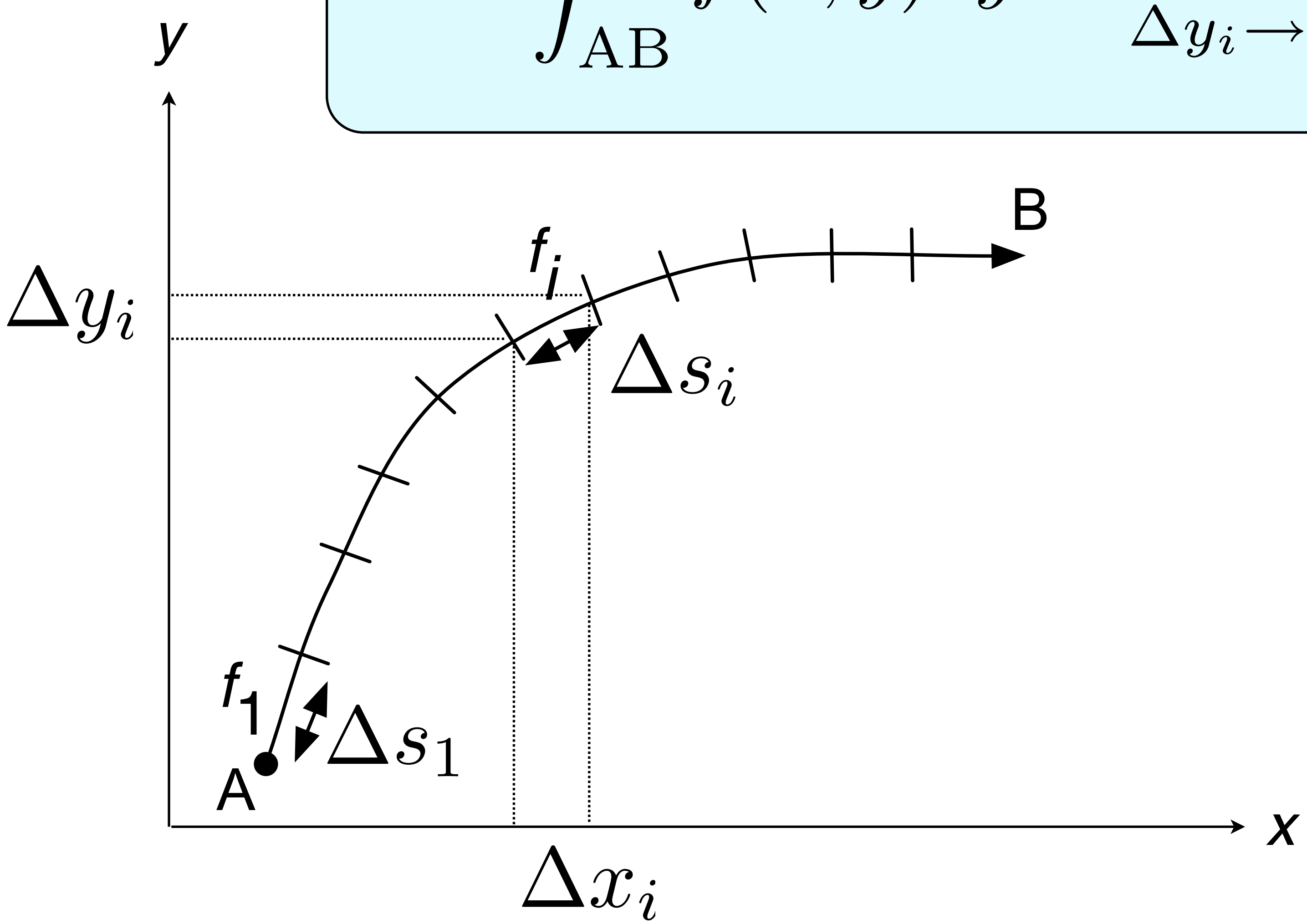
線積分 line integral

今, Δs_i のx軸，y軸への射影を$\Delta x_i, \Delta y_i$ とする。x軸と Δs_i なす角をαとすると,

$$\Delta x_i = \cos\alpha \Delta s_i, \Delta y_i = \sin\alpha \Delta s_i$$

$$\int_{\mathrm{AB}} f(x,y)dx \equiv \lim_{\Delta x_i \to 0} \sum_i f_i \Delta x_i$$

$$\int_{\mathrm{AB}} f(x,y)dy \equiv \lim_{\Delta y_i \to 0} \sum_i f_i \Delta y_i$$



で，x軸，y軸上への射影の線積分を定義する。

ここは高度なのでskipしていい

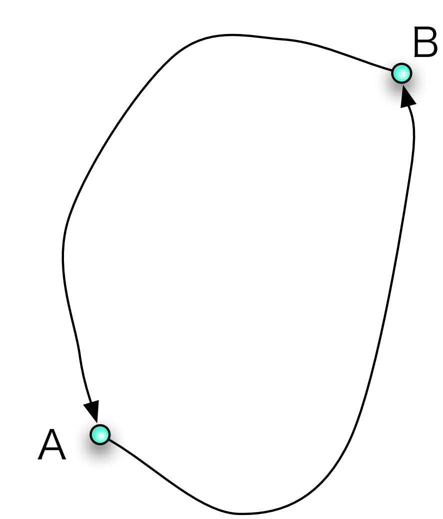
完全微分，不完全微分

exact differential, nonexact (imperfect) differential

$$df = P(x,y)dx + Q(x,y)dy$$

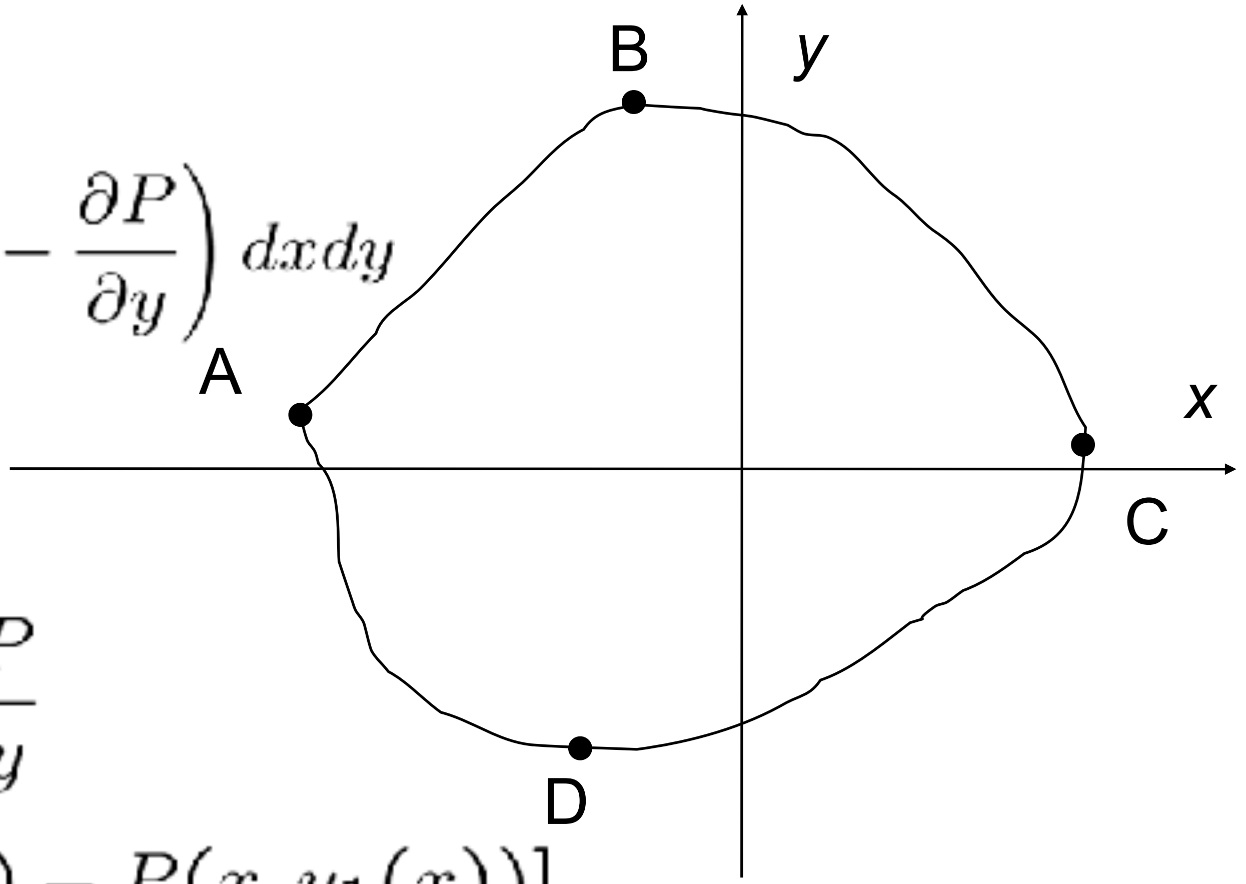
をある点Aから点Bまで*x*軸，*y*軸上への射影の線積分をする。
経路は，２次元平面内で自由にとれるが，積分が経路に依らないならば，
経路を任意にとってもとに戻る積分経路（経路が閉曲線）での
線積分はゼロになる。経路が閉曲線の場合，線積分を
以下のように書く。

$$\oint df$$



Green's Theorem

$$\oint_C [P(x,y)dx + Q(x,y)dy] = \int\int_R \left(\frac{\partial Q}{\partial x} - \frac{\partial P}{\partial y}\right) dxdy$$



Proof ABC : $y_2(x)$, ADC : $y_1(x)$

$$\int\int \frac{\partial P}{\partial y} dxdy = \int_{x_A}^{x_C} dx \int_{y_1(x)}^{y_2(x)} dy \frac{\partial P}{\partial y}$$
$$= \int_{x_A}^{x_C} dx [P(x, y_2(x)) - P(x, y_1(x))]$$
$$= -\oint dxP, \quad (C \text{ is a counterclockwise direction})$$

DAB : $x_2(y)$, DCB : $x_1(y)$

ここは高度なのでskipしていい

$$\int\int \frac{\partial Q}{\partial x} dxdy = \int_{y_D}^{y_B} dy \int_{x_2(y)}^{x_1(y)} dx \frac{\partial Q}{\partial x}$$
$$= \int_{y_D}^{y_B} dxQ(x_1(y), y) - Q(x_2(y), y)$$
$$= \oint dyQ, \quad (C \text{ is a counterclockwise direction})$$

$$\frac{\partial P}{\partial y} = \frac{\partial Q}{\partial x}$$

なら， $\oint df = 0$ となる。

$$\begin{aligned} df &= P(x,y)dx + Q(x,y)dy \\ &= \frac{\partial f}{\partial x}dx + \frac{\partial f}{\partial y}dy \end{aligned}$$

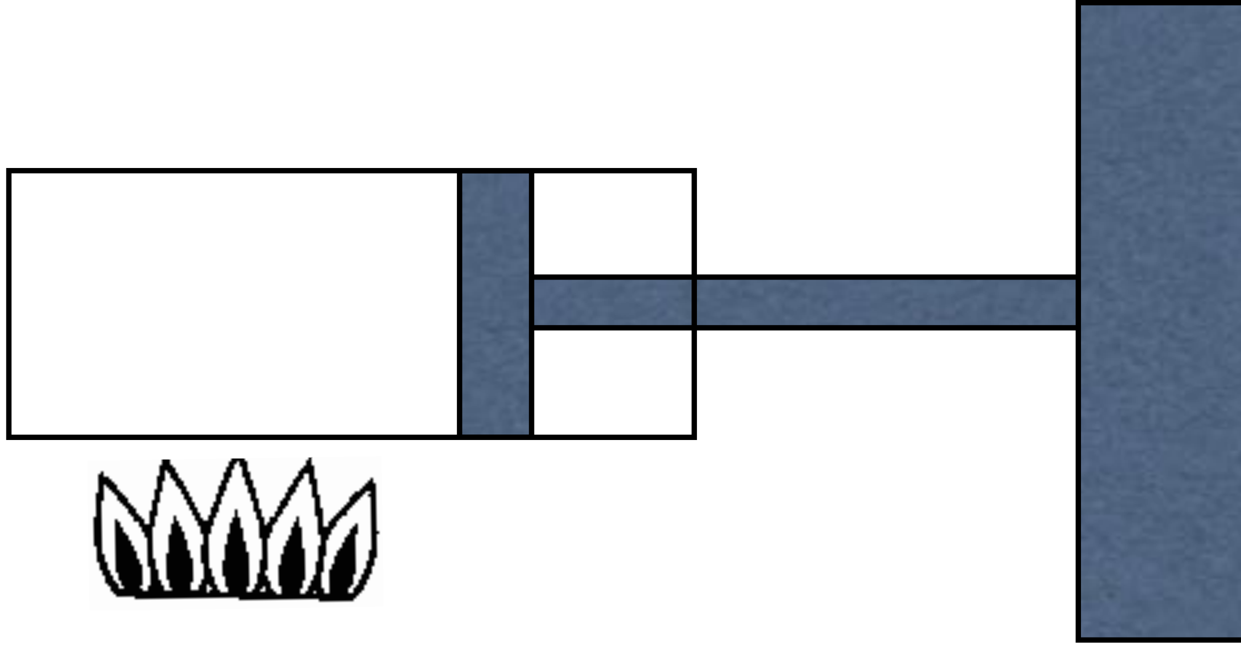
と書けるなら，完全微分が成立する上の式は

$$\frac{\partial}{\partial y}\frac{\partial f}{\partial x} = \frac{\partial}{\partial x}\frac{\partial f}{\partial y}$$

となる。

等容過程

isovolume



$$đW = -PdV = 0$$

$$dU = đQ + đW = đQ$$

$$\left(\frac{dU}{dT}\right)_V = \left(\frac{đQ}{dT}\right)_V = C_V(T)$$

$$(dU)_V = C_V(T)dT$$

$$\Delta U = \int_{T_1}^{T_2} C_V(T)dT$$

$$(dU)_V = dQ = C_V dT, \quad \left(\frac{\partial U}{\partial T}\right)_V = C_V$$

定容で温度を１度あげるのに必要な熱量

$$(dH)_P = dQ = C_P dT, \quad \left(\frac{\partial H}{\partial T}\right)_P = C_P$$

定圧で温度を１度あげるのに必要な熱量

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial (H + PV)}{\partial T}\right)_P$$

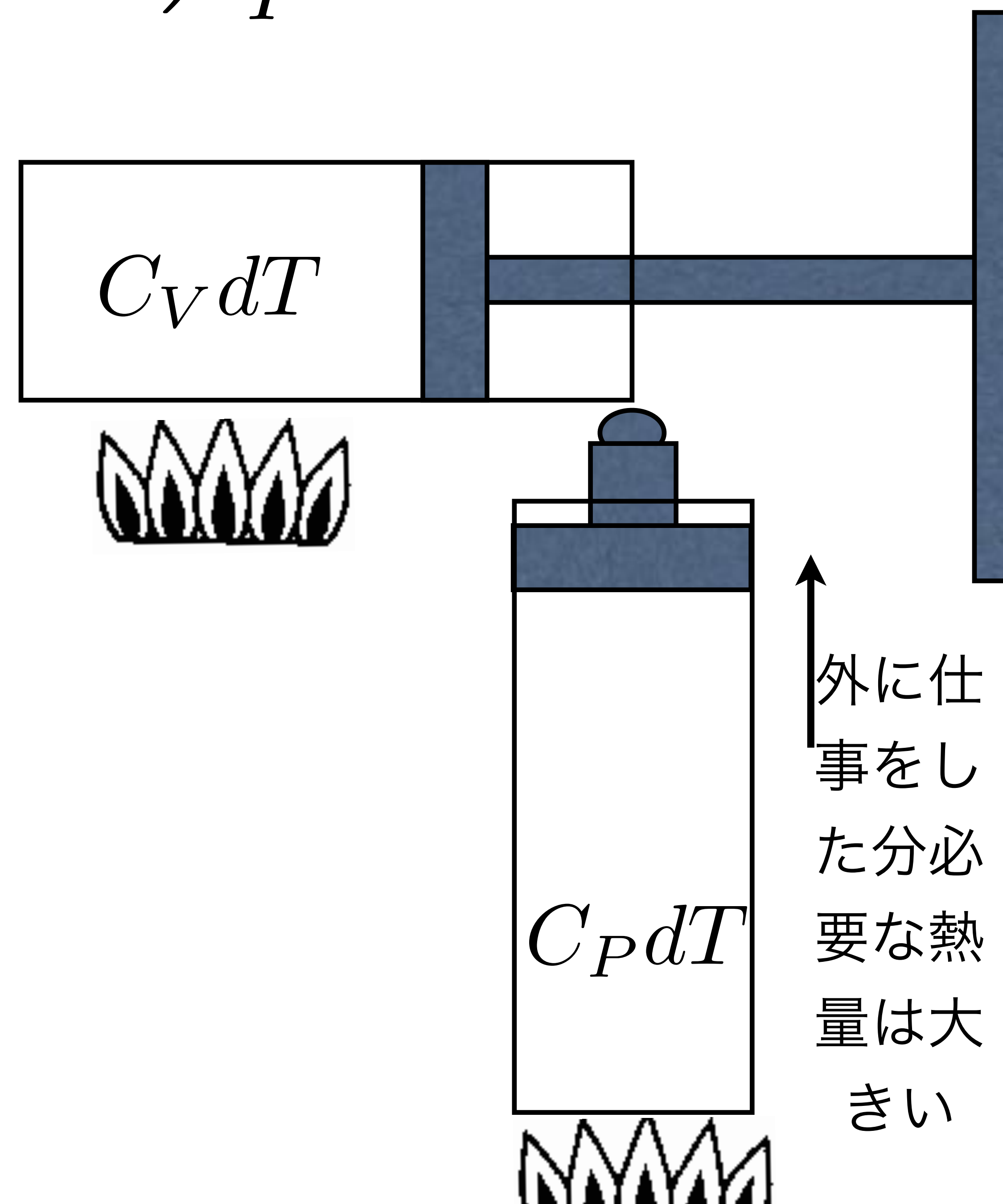
$$= \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P$$

$$PV = nRT, \ V = \frac{nRT}{P}$$

$$\left(\frac{\partial U}{\partial T}\right)_P = \frac{dU}{dT} = \left(\frac{\partial U}{\partial T}\right)_V = C_V$$

理想気体においてはUは温度だけの関数

$$C_P = C_V + nR$$



完全微分と不完全微分

$$(dU)_V = C_V(T)dT$$

内部エネルギーは温度だけの関数であるので

$$dU = C_V(T)dT$$

としてよい

$$dU = dQ - PdV$$

$$dQ = C_V(T)dT + PdV$$

$$dQ = C_V(T)dT + \frac{nRT}{V}dV$$

不完全微分 nonexact (imperfect) differential の例 はあるのか？

$$đQ = C_{\mathrm{V}}(T)dT + \frac{nRT}{V}dV$$

$$\frac{\partial C_{\mathrm{V}}(T)}{dV} = 0, \ \frac{\partial (nRT/V)}{\partial T} = \frac{nR}{V}$$

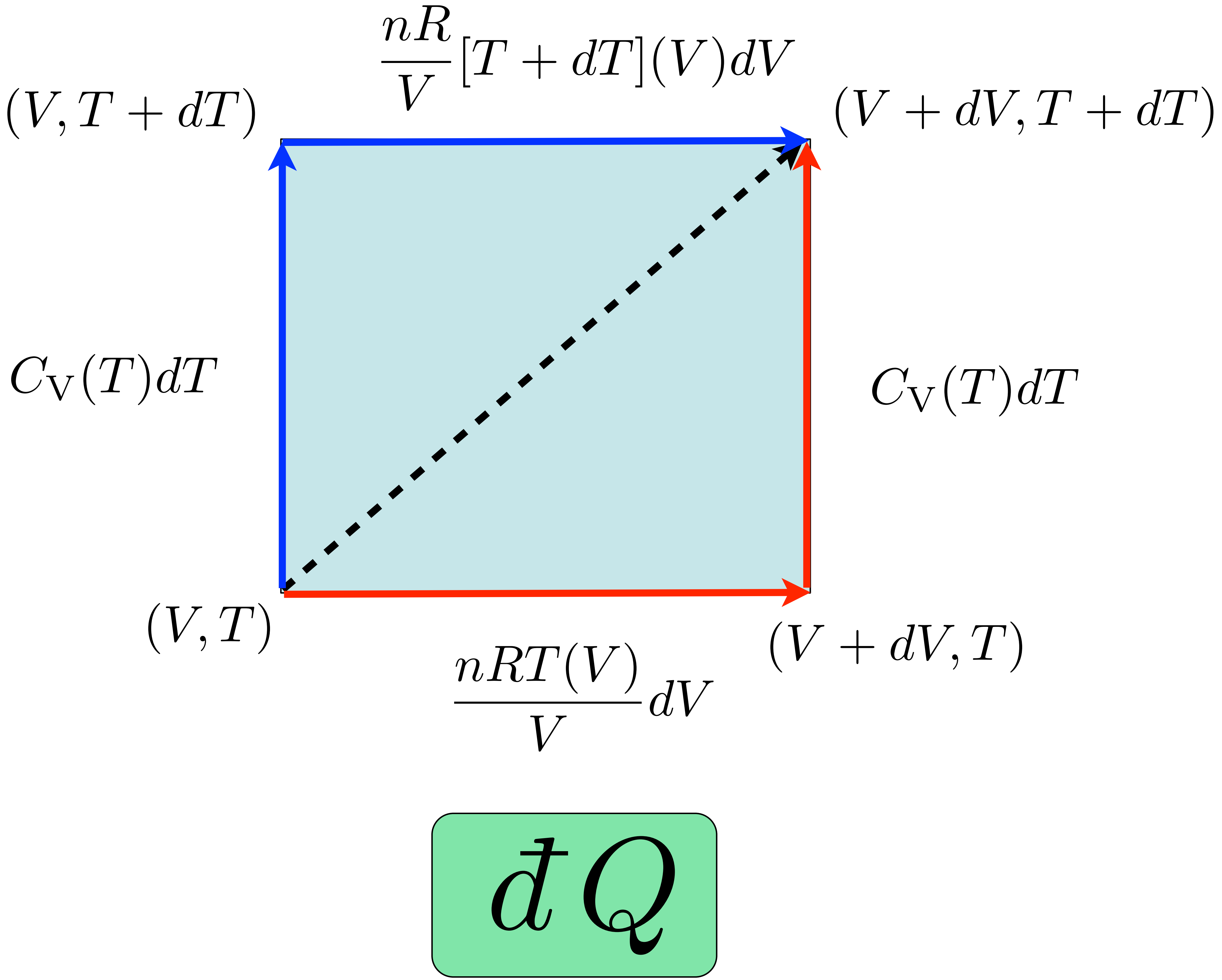
$$\rightarrow \mathrm{nonexact}$$

$$\frac{đQ}{T} = \frac{C_{\mathrm{V}}(T)}{T}dT + \frac{nR}{V}dV$$

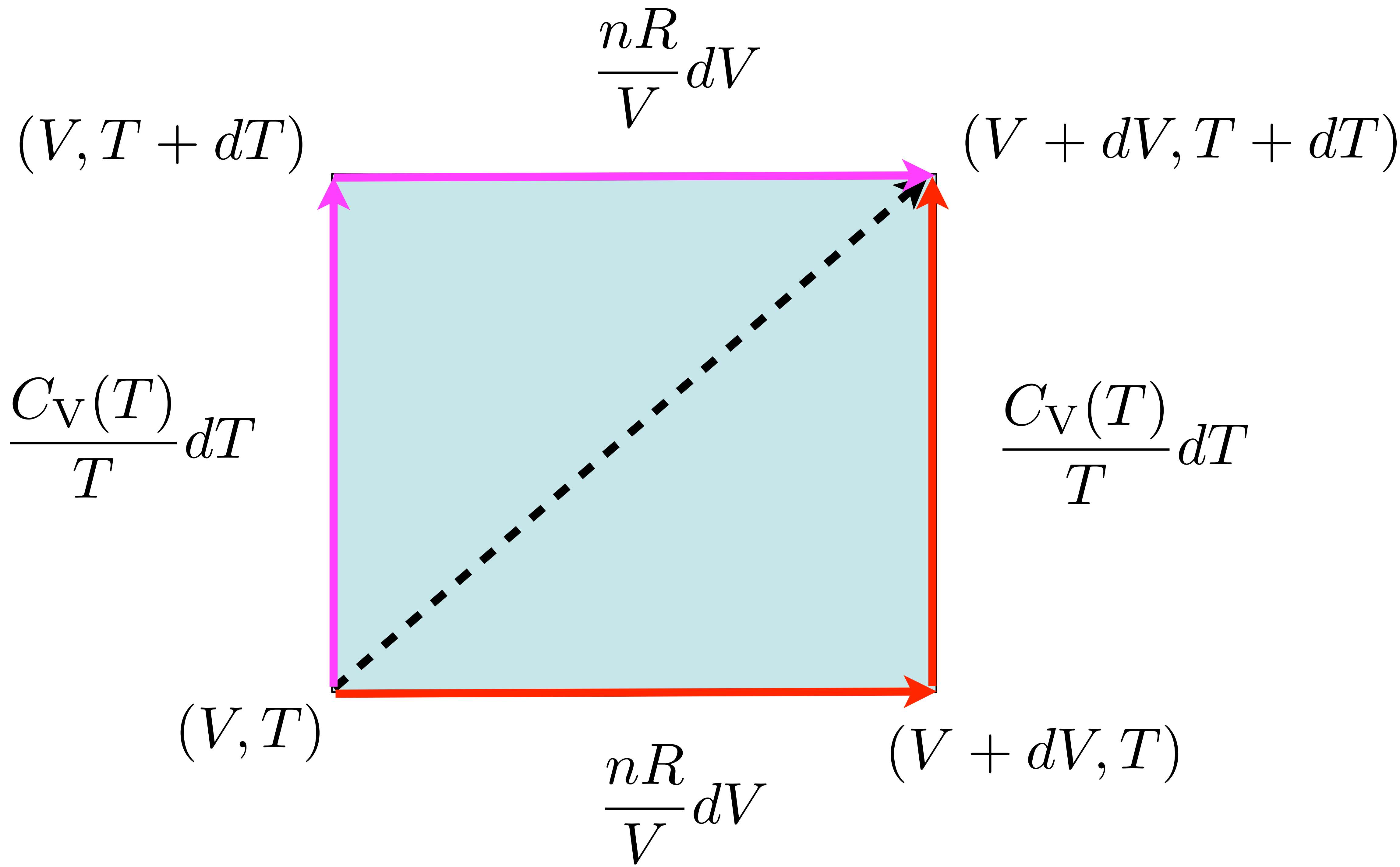
$$\frac{\partial (C_{\mathrm{V}}(T)/T)}{dV} = 0, \ \frac{\partial (nR/V)}{\partial T} = 0$$

$$\rightarrow \mathrm{exact}$$

McQuarrie and Simon, Appendix H.10



$\frac{nR}{V}[T+dT](V)dV$
$(V, T+dT)$
$(V+dV, T+dT)$
$C_{\mathrm{V}}(T)dT$
$C_{\mathrm{V}}(T)dT$
(V, T)
$(V+dV, T)$
$\frac{nRT(V)}{V}dV$
$đQ$


$\frac{nR}{V}dV$
$(V, T + dT)$
$(V + dV, T + dT)$
$\frac{C_{\mathrm{V}}(T)}{T}dT$
$\frac{C_{\mathrm{V}}(T)}{T}dT$
(V, T)
$(V + dV, T)$
$\frac{nR}{V}dV$

$$\frac{đQ}{T}$$

よく使われる偏微分の関係式

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

$$P \Leftrightarrow V \Leftrightarrow T$$

$$f(x, y) - z = 0 \quad \Rightarrow F(x, y, z) = 0$$

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy \qquad (*)$$

$y = g(z, x)$ とすれば

$$dy = \left(\frac{\partial y}{\partial z}\right)_x dz + \left(\frac{\partial y}{\partial x}\right)_z dx$$

このdyを（＊）のdyに代入すると

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x \left[\left(\frac{\partial y}{\partial z}\right)_x dz + \left(\frac{\partial y}{\partial x}\right)_z dx\right]$$

まとめると

$$0=\left[\left(\frac{\partial z}{\partial x}\right)_y+\left(\frac{\partial z}{\partial y}\right)_x\left(\frac{\partial y}{\partial x}\right)_z\right]dx+\left[\left(\frac{\partial z}{\partial y}\right)_x\left(\frac{\partial y}{\partial z}\right)_x-1\right]dz$$

すべてのz, xで成立するには,

$$\left(\frac{\partial z}{\partial x}\right)_y+\left(\frac{\partial z}{\partial y}\right)_x\left(\frac{\partial y}{\partial x}\right)_z=0 \qquad (**)$$

$$\left(\frac{\partial z}{\partial y}\right)_x\left(\frac{\partial y}{\partial z}\right)_x-1=0 \qquad (***)$$

（＊＊＊）より

$$\left(\frac{\partial z}{\partial y}\right)_x=\frac{1}{\left(\frac{\partial y}{\partial z}\right)_x}$$

$$(**) \times \left(\frac{\partial x}{\partial z}\right)_y$$

$$\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial z}\right)_y + \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z \left(\frac{\partial x}{\partial z}\right)_y = 0$$

$$\left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z \left(\frac{\partial x}{\partial z}\right)_y = -\frac{\left(\frac{\partial z}{\partial x}\right)_y}{\left(\frac{\partial z}{\partial x}\right)_y} = -1$$

$$\boxed{\left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z \left(\frac{\partial x}{\partial z}\right)_y = -1}$$

$$\left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z \left(\frac{\partial x}{\partial z}\right)_y = -1$$

x, *y*, *z*

は

P, *V*, *T*

$$\left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V = -1$$

$$(V\beta)^{-1}(-V\kappa)\left(\frac{\partial P}{\partial T}\right)_V = -1$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{\beta}{\kappa}$$

偏微分のchainルール

$$u = f(x, y), \quad x = x(t), \quad y = y(t), \quad f(x(t), y(t)) = U(t)$$

$$[u = xy, \quad x = e^{-t}, \quad y = t^2, \quad U(t) = t^2 e^{-t}\ ]$$

$$\begin{aligned}
\Delta u &= f(x + \Delta x, y + \Delta y) - f(x, y) \\
&= [f(x + \Delta x, y + \Delta y) - f(x, y + \Delta y)] - [f(x, y + \Delta y) - f(x, y)] \\
&= \left. f_x \right|_{y + \Delta y} \Delta x + \left. f_y \right|_x \Delta y
\end{aligned}$$

$$\frac{\Delta u}{\Delta t} = \left. f_x \right|_{y + \Delta y} \frac{\Delta x}{\Delta t} + \left. f_y \right|_x \frac{\Delta y}{\Delta t}$$

$$\frac{du}{dt} = \frac{dU}{dt} = \left(\frac{\partial u}{\partial x} \right)_y \frac{dx}{dt} + \left(\frac{\partial u}{\partial y} \right)_x \frac{dy}{dt}$$

$t = x$

$$u = f(x,y), \quad y = y(x), \quad f(x, y(x)) = U(x)$$

$$[u = xy, \quad y = x^2, \quad U(x) = x^3 \,]$$

$$\frac{du}{dx} = \frac{dU}{dx} = \left(\frac{\partial u}{\partial x}\right)_y \frac{dx}{dx} + \left(\frac{\partial u}{\partial y}\right)_x \frac{dy}{dx}$$

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

$$\frac{du}{dx} = y + x(2x) = x^2 + 2x^2 = 3x^2$$

拡張版

$$u = f(x,y), \quad x = x(s,t), \quad y = y(s,t), \quad f(x(s,t), y(s,t)) = U(s,t)$$

$$[u = xy, \quad x = se^{-t}, \quad y = \ln se^{-t}, \quad U(s,t) = s \ln se^{-2t} \ ]$$

$$\begin{aligned}
\Delta u &= f(x+\Delta x, y+\Delta y) - f(x,y) \\
&= [f(x+\Delta x, y+\Delta y) - f(x, y+\Delta y)] - [f(x, y+\Delta y) - f(x,y)] \\
&= \left. f_x \right|_{y+\Delta y} \Delta x + \left. f_y \right|_x \Delta y \\
\frac{\Delta u}{\Delta t} &= \left. f_x \right|_{y+\Delta y} \frac{\Delta x}{\Delta t} + \left. f_y \right|_x \frac{\Delta y}{\Delta t} \\
\left(\frac{\partial U}{\partial t}\right)_s &= \left(\frac{\partial u}{\partial x}\right)_y \left(\frac{\partial x}{\partial t}\right)_s + \left(\frac{\partial u}{\partial y}\right)_x \left(\frac{\partial y}{\partial t}\right)_s \\
\frac{\Delta u}{\Delta s} &= \left. f_x \right|_{y+\Delta y} \frac{\Delta x}{\Delta s} + \left. f_y \right|_x \frac{\Delta y}{\Delta s} \\
\left(\frac{\partial U}{\partial s}\right)_t &= \left(\frac{\partial u}{\partial x}\right)_y \left(\frac{\partial x}{\partial s}\right)_t + \left(\frac{\partial u}{\partial y}\right)_x \left(\frac{\partial y}{\partial s}\right)_t
\end{aligned}$$

例

$$u = f(x, y), \quad x = x(s, t), \quad y = y(s, t), \quad f(x(s,t), y(s,t)) = U(s, t)$$

$$[u = xy, \quad x = se^{-t}, \quad y = \ln se^{-t}, \quad U(s,t) = s \ln se^{-2t}\ ]$$

$$\left(\frac{\partial U}{\partial t}\right)_s = \left(\frac{\partial u}{\partial x}\right)_y \left(\frac{\partial x}{\partial t}\right)_s + \left(\frac{\partial u}{\partial y}\right)_x \left(\frac{\partial y}{\partial t}\right)_s$$

$$s \ln s(-2)e^{-2t} = ys(-1)e^{-t} + x \ln s(-1)e^{-t} = -\ln se^{-t}se^{-t} - se^{-t}\ln se^{-t}$$

$$= -s \ln se^{-2t} - s \ln se^{-2t} = -2s \ln se^{-2t}$$

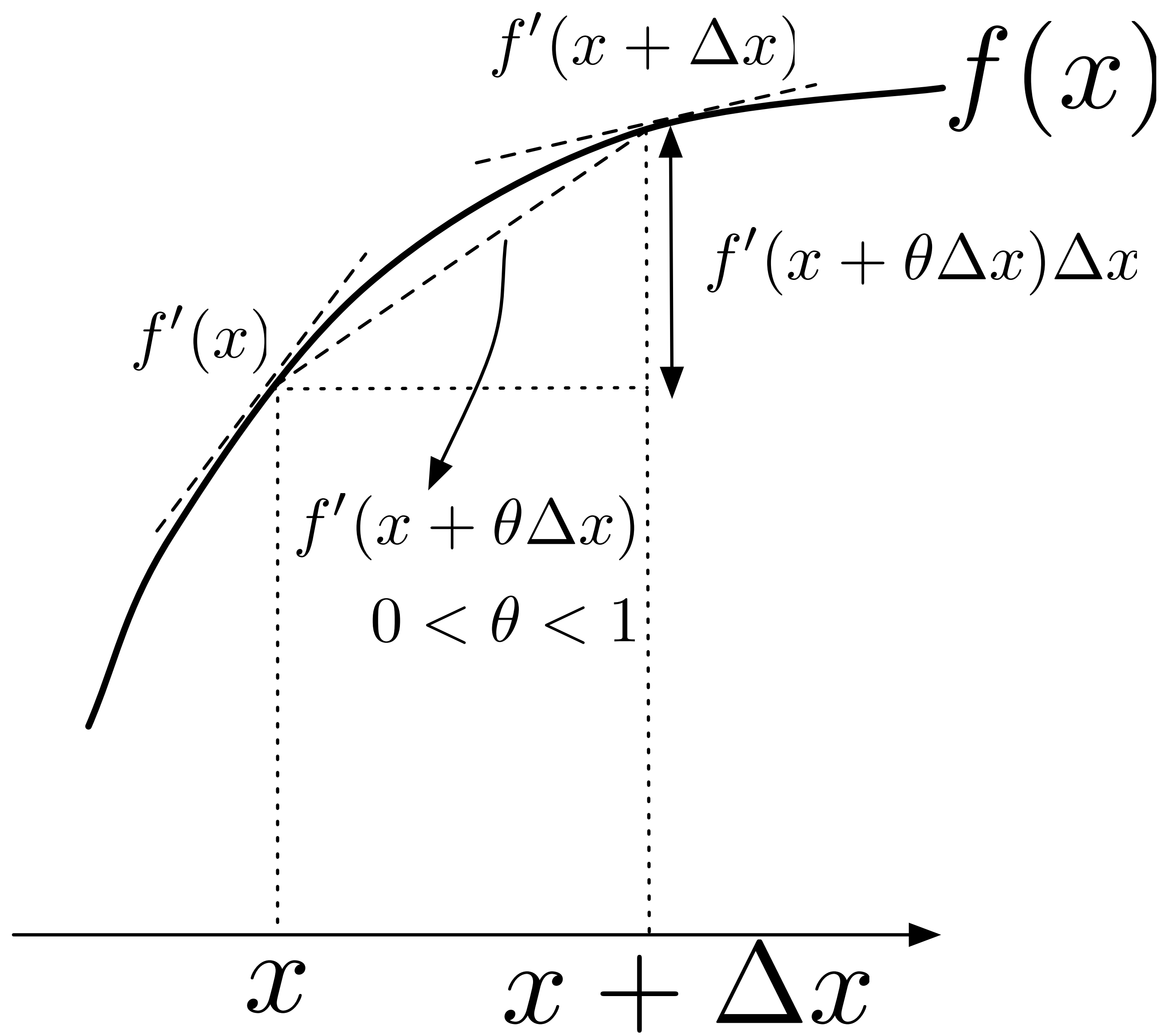
$$\left(\frac{\partial U}{\partial s}\right)_t = \left(\frac{\partial u}{\partial x}\right)_y \left(\frac{\partial x}{\partial s}\right)_t + \left(\frac{\partial u}{\partial y}\right)_x \left(\frac{\partial y}{\partial s}\right)_t$$

$$(\ln s + 1)e^{-2t} = ye^{-t} + x\frac{1}{s}e^{\ t} = \ln se^{-t}e^{-t} + se^{-t}\frac{1}{s}e^{-t} = (\ln s + 1)e^{-2t}$$

より厳密には

微分　differentiation

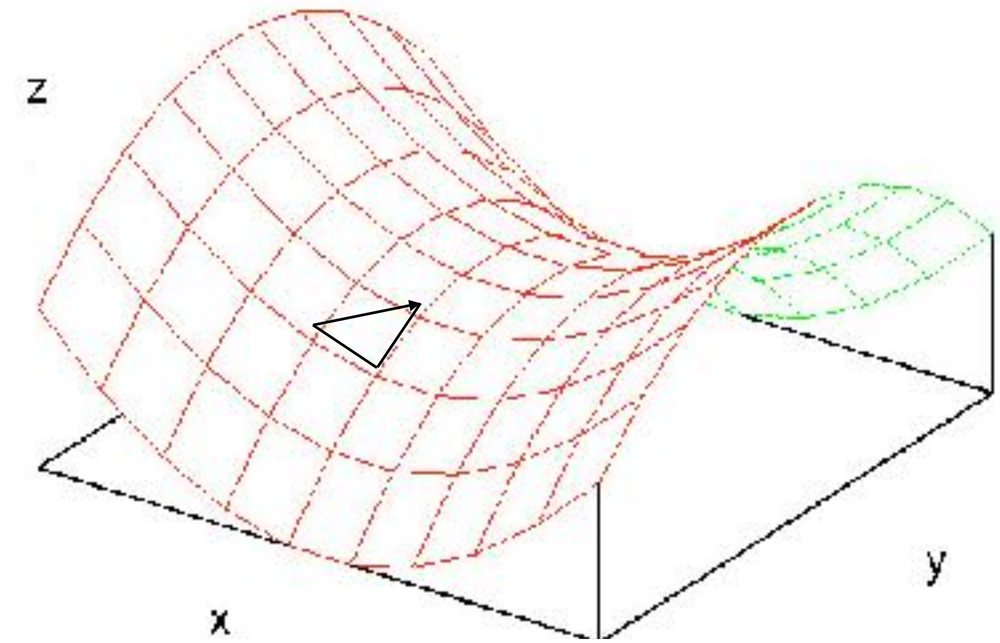
$$\frac{df(x)}{dx} = f'(x) = \lim_{\Delta x \to 0} \frac{f(x+\Delta x) - f(x)}{\Delta x}$$



$$f(x+\Delta x) - f(x) \simeq f'(x+\theta\Delta x)\Delta x$$

Total 全微分　and

Partial Differentials　偏微分



$$
\begin{aligned}
\Delta f &= f(x+\Delta x, y+\Delta y) - f(x,y) \\
&= [f(x+\Delta x, y+\Delta y) - f(x, y+\Delta y)] + [f(x, y+\Delta y) - f(x,y)] \\
&= f_x(x+\theta_1\Delta x, y+\Delta y)\Delta x + f_y(x, y+\theta_2\Delta y)\Delta y, \quad (0 < \theta_1, \theta_2 < 1) \\
&= f_x(x,y)\Delta x + f_y(x,y)\Delta y + \epsilon_1\Delta x + \epsilon_1\Delta y
\end{aligned}
$$

$$
\begin{aligned}
f_x &= \frac{\partial f}{\partial x} = \lim_{\Delta x \to 0} \frac{f(x+\Delta x, y) - f(x,y)}{\Delta x} \\
f_y &= \frac{\partial f}{\partial y} = \lim_{\Delta y \to 0} \frac{f(x, y+\Delta y) - f(x,y)}{\Delta y} \\
\epsilon_1 &\equiv f_x(x+\theta_1\Delta x, y+\Delta y) - f_x(x,y) \\
\epsilon_2 &\equiv f_y(x, y+\theta_2\Delta y) - f_y(x,y)
\end{aligned}
$$

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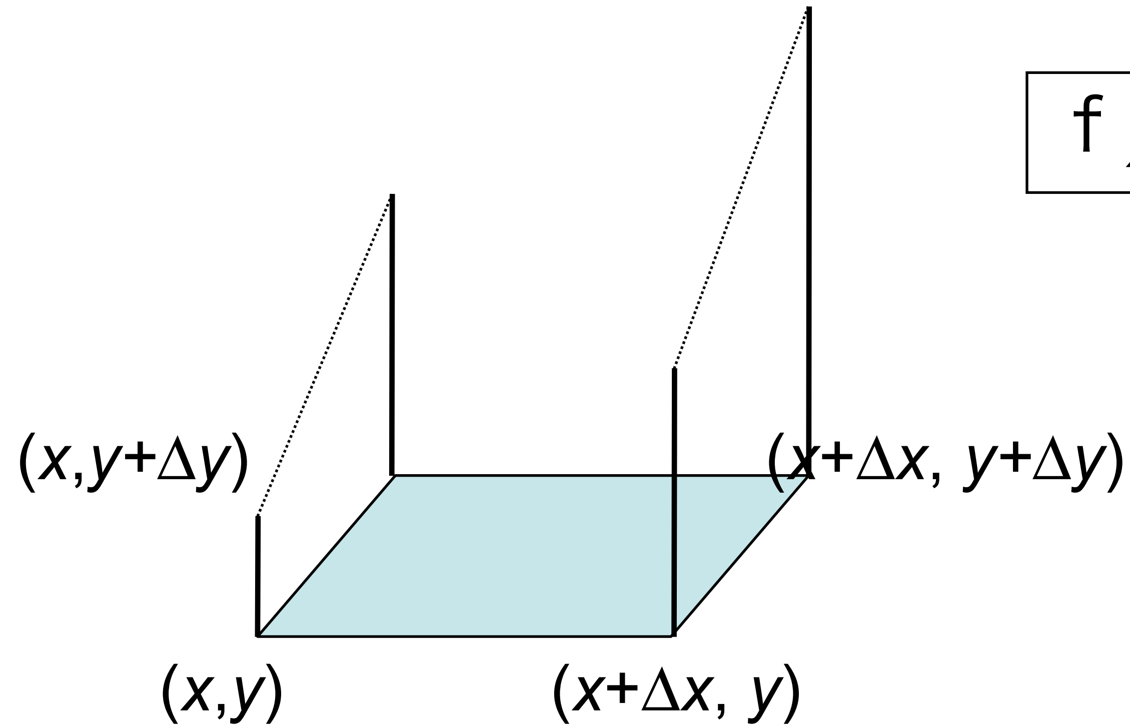
$$
df = f_x(x,y)dx + f_y(x,y)dy = \frac{\partial f}{\partial x}dx + \frac{\partial f}{\partial y}dy
$$

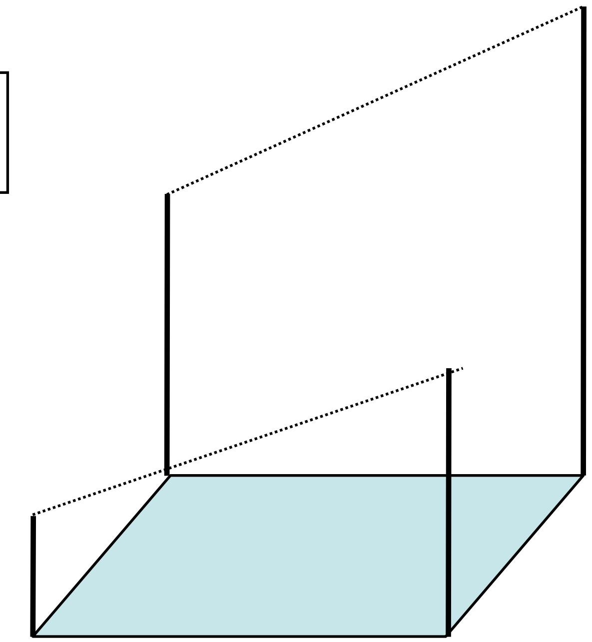
全微分（第一階全微分）

$f_{xy} = f_{yx}$ の証明

$$F = f(x+\Delta x, y+\Delta y) - f(x+\Delta x, y) - [f(x, y+\Delta y) - f(x,y)]$$



$$F = f(x+\Delta x, y+\Delta y) - f(x, y+\Delta y) - [f(x+\Delta x, y) - f(x,y)]$$



$$\varphi(x) = f(x, y+\Delta y) - f(x,y)$$
$$\varphi'(x) = f_x(x, y+\Delta y) - f_x(x,y)$$

$$\begin{aligned} F &= \varphi(x+\Delta x) - \varphi(x) \\ &= \Delta x \varphi'(x+\theta\Delta x) \\ &= \Delta x \{f_x(x+\theta\Delta x, y+\Delta y) - f_x(x+\theta\Delta x, y)\} \\ &= \Delta x \Delta y f_{xy}(x+\theta\Delta x, y+\theta'\Delta y) \end{aligned}$$

$$\phi(y) = f(x+\Delta x, y) - f(x,y)$$
$$\phi'(y) = f_y(x+\Delta x, y) - f_y(x,y)$$

$$\begin{aligned} F &= \phi(y+\Delta y) - \phi(y) \\ &= \Delta y \phi'(y+\theta_1\Delta y) \\ &= \Delta y \{f_y(x+\Delta x, y+\theta_1\Delta y) - f_y(x, y+\theta_1\Delta y)\} \\ &= \Delta x \Delta y f_{yx}(x+\theta'_1\Delta x, y+\theta_1\Delta y) \end{aligned}$$

$$\Delta x, \Delta y \to 0, \quad f_{xy} = f_{yx}$$

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高次の展開（ここは省略可）

$$\begin{aligned}\Delta f &= f(x+\Delta x, y+\Delta y) - f(x,y)\\ &= [f(x+\Delta x, y+\Delta y) - f(x, y+\Delta y)]\\ &\quad +[f(x, y+\Delta y) - f(x,y)]\end{aligned}$$

$$\begin{aligned}f(x+\Delta x, y+\Delta y) - f(x, y+\Delta y) &= \Delta x f_x(x, y+\Delta y) + \frac{(\Delta x)^2}{2} f_{xx}(x+\theta_1\Delta x, y+\Delta y)\\ &= \Delta x\left\{f_x(x,y) + \Delta y f_{xy}(x, y+\theta_2\Delta y)\right\}\\ &\quad +\frac{(\Delta x)^2}{2} f_{xx}(x+\theta_1\Delta x, y+\Delta y)\\ f(x, y+\Delta y) - f(x,y) &= \Delta y f_y(x,y) + \frac{(\Delta y)^2}{2} f_{yy}(x, y+\theta_3\Delta y)\end{aligned}$$

$$\begin{aligned}\Delta f &= \{\Delta x f_x(x,y) + \Delta y f_y(x,y)\}\\ &\quad +\frac{1}{2}\Big\{(\Delta x)^2 f_{xx}(x+\theta_1\Delta x, y+\Delta y) + 2\Delta x\Delta y f_{xy}(x, y+\theta_2\Delta y)\\ &\quad +(\Delta y)^2 f_{yy}(x, y+\theta_3\Delta y)\Big\}\end{aligned}$$

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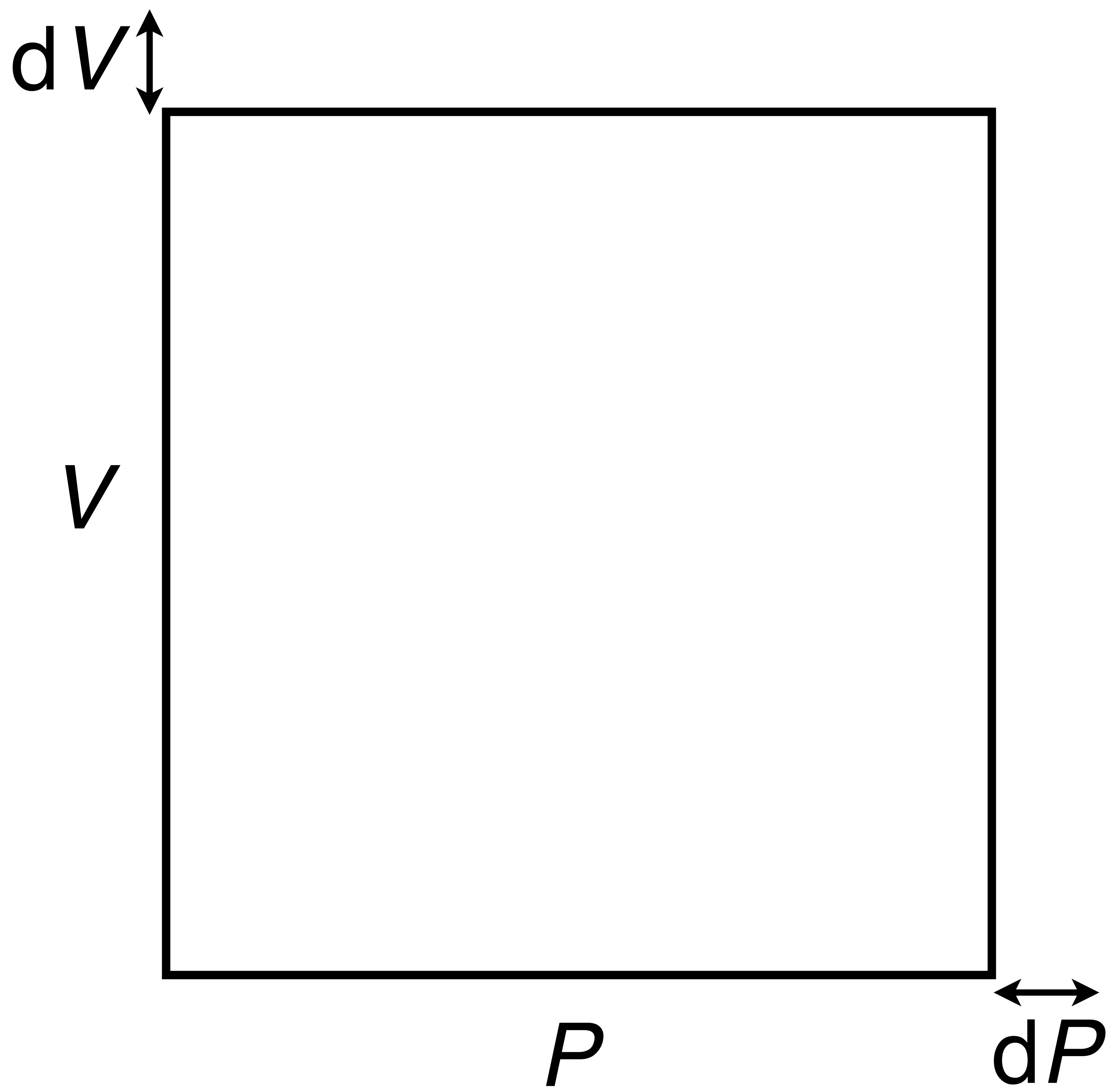
$$\begin{aligned}\Delta f &= df + \frac{1}{2}d^2 f\\ df &= \frac{\partial f}{\partial x}dx + \frac{\partial f}{\partial y}dy\\ d^2 f &= \frac{\partial^2 f}{\partial x^2}dx^2 + 2\frac{\partial^2 f}{\partial xy}dxdy + \frac{\partial^2 f}{\partial y^2}dy^2\end{aligned}$$

$\rightarrow$ 第二階全微分

$$d(PV) = VdP + PdV$$ の証明

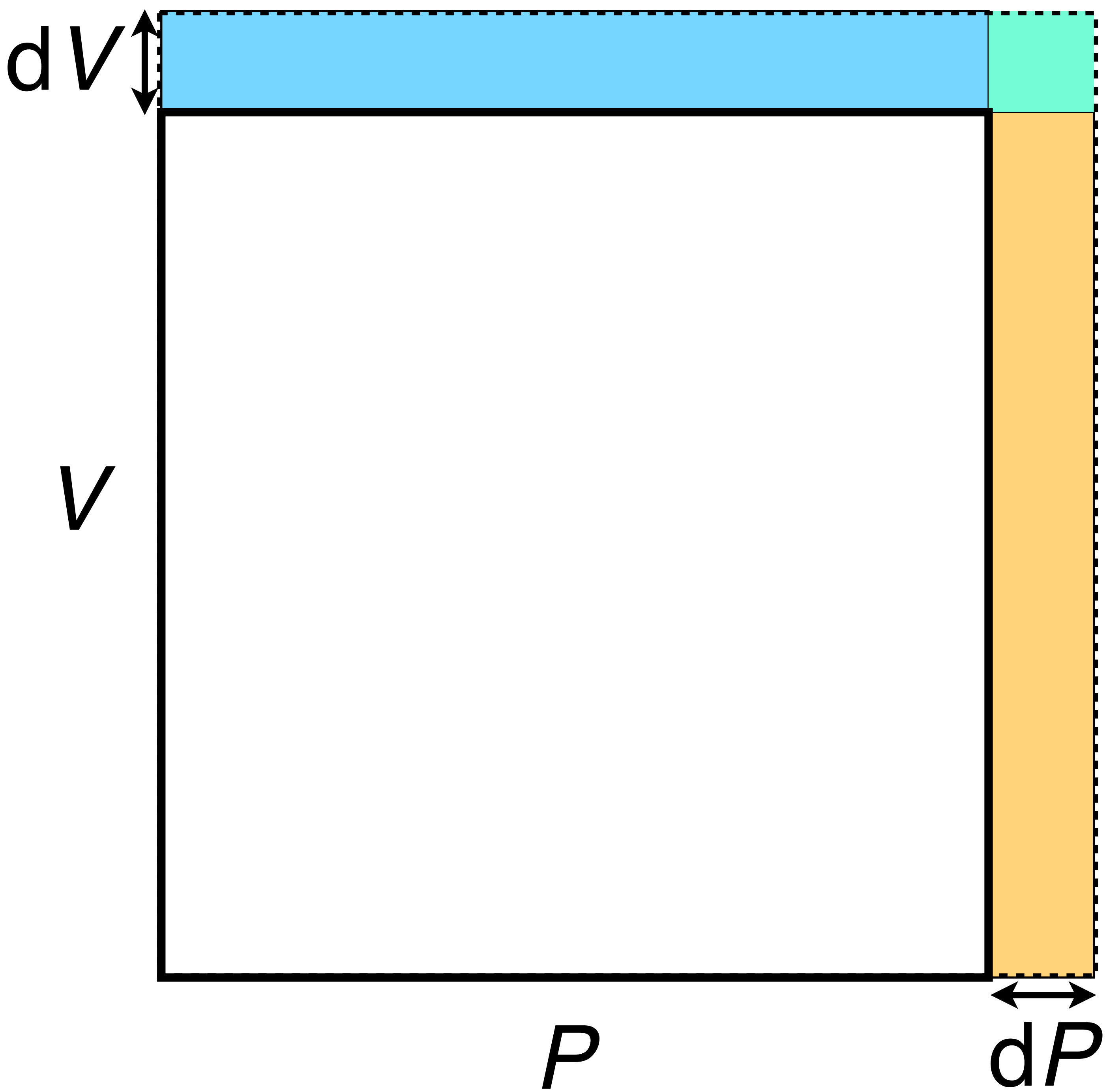
$$(P+dP)(V+dV) = \boxed{PV} + PdV + Vdp + dPdV$$



$$d(PV) = VdP + PdV$$ の証明

$$(P+dP)(V+dV) = \boxed{PV} + PdV + Vdp + dPdV$$

↑微少量
無視する



d(*PV*) ≡
(*P*+d*P*)(*V*+d*V*) - *PV*
= 点線の四角と
実線の四角の
面積の差

d(*PV*) = *P*d*V*+*V*d*P*