Conversion of PDF from particle average to atom average

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- Particle size distribution (PDF) measured by TEM is usually a particle average PDF.
- In XAS, The average spectrum is and atom average of all the sites.
- Therefore, the particle size obtained from TEM and particle size obtained from XAS will be different. (*Annu. Rev. Anal. Chem.* **2011**. *4*, 23–39)
- Here, we will discuss how to convert the particle average PDF to atom average PDF.

Assumptions

- The particle is spherical.

$$V(r) = \frac{4}{3}\pi r^3$$

$$V(D) = \frac{1}{6}\pi D^3$$

- The particle size distribution is normal distribution.

$$f(D) = \frac{1}{\sqrt{2\pi}\sigma}\exp\left(-\frac{(D-\mu)^2}{2\sigma^2}\right)$$

Conversion

When $g(D)$ is the probability density function of particle size distribution scaled by $V(D)$, the conversion of $f(D)$ to $g(D)$ is given by

$$g(D) = \frac{V(D)f(D)}{\int_{-\infty}^{\infty} V(D)f(D)dD}$$

The expectation and variance of $g(D)$ are given by

$$\mu = \int_{-\infty}^{\infty} Dg(D)dD$$

$$\begin{aligned}\sigma^2 &= \int_{-\infty}^{\infty} (D-\mu)^2 g(D)dD \\ &= \int_{-\infty}^{\infty} D^2 g(D)dD - \mu^2\end{aligned}$$

Calculation of normalization factor

The integrals were performed using Wolfram Mathematica 12.3.1. The results are given below.

$$\int_{-\infty}^{\infty} V(D) f(D) dD = \frac{1}{\sqrt{2\pi}\sigma} \int_{-\infty}^{\infty} \frac{1}{6}\pi D^3 \exp\left(-\frac{(D-\mu)^2}{2\sigma^2}\right) dD$$
$$= \frac{\pi}{6}\mu(\mu^2 + 3\sigma^2)$$

Mathematica ouput:

```
Integrate[1/6*Pi*x^3/(sigma Sqrt[2*Pi]) Exp[-1/2*((x-mu)/sigma)^2], {x, -Infinity, Infinity}]
```

Out[106]= $\dfrac{\text{mu}\,\pi\,(\text{mu}^2 + 3\,\text{sigma}^2)}{6\sqrt{\frac{1}{\text{sigma}^2}}\,\text{sigma}}$ if $\text{Re}[\text{sigma}^2] \geq 0$

ConditionalExpression

g(D)

$$g(D) = \frac{x^3}{\mu(\mu^2 + 3\sigma^2)\sqrt{2\pi\sigma}} \exp\left(-\frac{(D-\mu)^2}{2\sigma^2}\right)$$

Calculation of expectation

$$\mu = \int_{-\infty}^{\infty} Dg(D)dD$$

$$= \frac{\mu^4 + 6\mu^2\sigma^2 + 3\sigma^4}{\mu(\mu^2 + 3\sigma^2)}$$

Mathematica output:

```
In[50]:= Integrate[x * 1/6*Pi*x^3/(sigma Sqrt[2*Pi]) Exp[-1/2 * ((x - mu)/sigma)^2], {x, -Infinity, Infinity}] / (1/6 mu π (mu^2 + 3 sigma^2))
```

Out[50]= $\frac{\text{mu}^4 + 6\,\text{mu}^2\,\text{sigma}^2 + 3\,\text{sigma}^4}{\text{mu}\sqrt{\frac{1}{\text{sigma}^2}}\,\text{sigma}\,(\text{mu}^2 + 3\,\text{sigma}^2)}$ if $\text{Re}[\text{sigma}^2] \geq 0$

Calculation of variance

$$\sigma^2 = \int_{-\infty}^{\infty} D^2 g(D) dD - \mu^2$$

$$= \frac{\mu^4 + 10\mu^2\sigma^2 + 15\sigma^4}{\mu^2 + 3\sigma^2} - \mu^2$$

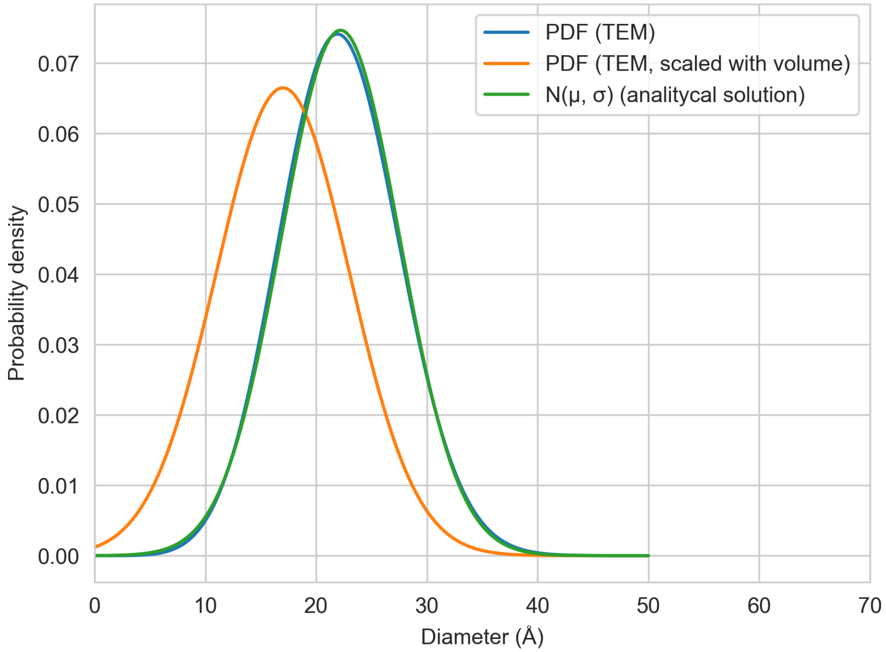
Mathematica output:

```
In[50]:= Integrate[x * 1/6*Pi*x^3/(sigma Sqrt[2*Pi]) Exp[-1/2 * ((x - mu)/sigma)^2], {x, -Infinity, Infinity}]/(1/6 mu π (mu^2 + 3 sigma^2))
```

$$\text{Out[50]=} \quad \frac{mu^4 + 6\, mu^2\, sigma^2 + 3\, sigma^4}{mu \sqrt{\frac{1}{sigma^2}}\, sigma\, (mu^2 + 3\, sigma^2)} \quad \text{if } Re[sigma^2] \geq 0$$

Mock example

$$\mu = 17\mathring{A}, \sigma = 6\mathring{A}$$



Conclusion

- The conversion of particle average PDF to atom average PDF obtained by 2 assumptions.
    - The particle is spherical.
    - The particle size distribution is normal distribution.
- The converted μ and σ are given by

$$\mu = \frac{\mu^4 + 6\mu^2\sigma^2 + 3\sigma^4}{\mu(\mu^2 + 3\sigma^2)}$$

$$\sigma^2 = \frac{\mu^4 + 10\mu^2\sigma^2 + 15\sigma^4}{\mu^2 + 3\sigma^2} - \mu^2$$

Python code

```python
def mu_vol(mu, sigma):
    return (mu**4 + 6*mu**2*sigma**2 + 3*sigma**4)/(mu*(mu**2 + 3*sigma**2))

def sigma_vol(mu, sigma):
    return np.sqrt((mu**4 + 10 * mu**2 * sigma**2 +  15 * sigma**4)/(mu**2 + 3*sigma**2) - mu_vol(mu, sigma)**2)
```