**Introduction:**

- concept of diameter,
- mobility and mobility model,
- basic theoretical models,
- who made the Millikan model?
- ISO15900,
- updating the Millikan model,
- why the new models don’t have success?

**Nanoparticles have “atmospheres”, no solid surface**

Density functions of two colliding nanoparticles

**Mobility and mobility model**

Precondition: the mean drift velocity $v$ is proportional to the drag force $F$.

Mechanical mobility $B = v/F$, electrical mobility $Z = v/E$

$F = EqF$ follows in $Z = qB$. We have $q = e$ and $Z = eB$.

A model of mobility is an algorithm that uses parameters of the particle and the air (pressure, temperature, diameter, etc.) and issues an estimate of the particle mobility:

$$Z = Z_0 = f_0(p, T, d) \quad \text{or} \quad Z = Z_0 = f_0(p, T, \ldots, d).$$

The inverse model $d = d_0 = g_0(p, T, Z)$ is to be mathematically derived from the direct algorithm.

**Theoretical basic models**

The Newton model of drag is nonlinear

$$F = c \frac{v^2}{2} \frac{d_0}{4}$$

Speed and fictive mechanical mobility

$$v = \sqrt{FF}$$

Stokes model of drag is linear

$$F = 3\pi\eta d v$$

Rigid sphere model by Chapman ja Enskog

in first approximation $\Omega = \Omega^{(0)}$ and $\Omega^{(1)} = \Omega^{(2)} = \pi r^2$

$$B = \frac{3}{2(d + d_0)} \frac{1 + \frac{m}{m_0}}{2\pi n_0 kT}$$

Einstein (1924) calculated effect of diffuse impacts on drag of about $d = 1.33$

**A selection of diameters**

[Image]

**Mass diameter**

$$d = \frac{3}{2\eta} \sqrt{\frac{6m}{\pi\rho}}$$

NB: $\rho \neq$ density of bulk matter

$\rho = $ density of particle matter

An array of packed spheres has the density of 0.52 $\rho$ in case of the simple cubic lattice and 0.74 $\rho$ in case of the closest packing.


**Mobility diameter**

Mobility diameter is defined as the diameter of a hard sphere of the same mobility as the considered particle. Thus the mobility diameter of a spherical particle is just the same as its geometric diameter.

Sometimes the mobility diameter is considered as a value $d_0$ issued by a specific mobility model

$$d_0 = g_0(p, T, Z),$$

where $g_0$ is inverse function of the model $M$ and $Z$ is measured mobility. The choice of the specific model is free, one could choose even plain Stokes or Newton. Thus $d_0$ should not be considered as a physical quantity. It is a specific estimate of the diameter.
There is no likelihood man can ever tap the power of the atom. The glib supposition of utilizing atomic energy when our coal has run out is a completely unscientific Utopian dream, a childish bug-a-boo. Nature has introduced a few fool-proof devices into the great majority of elements that constitute the bulk of the world, and they have no energy to give up in the process of disintegration.
(Pseudo)problem of free path

\[ Z = \left( 1 + Kn \left( \frac{A + B \exp \left( \frac{-C}{Kn} \right)}{3 \pi \eta d} \right) \right) \frac{q}{3 \pi \eta d} \]

In old books \( l = 3D/\nu = 90 \text{ nm} \), in new books \( l = 2D/\nu = 60 \text{ nm} \)

\[ Z = \left( 1 + \frac{2}{d} \left( \frac{A + B \exp \left( \frac{-C}{d} \right)}{3 \pi \eta d} \right) \right) \frac{q}{3 \pi \eta d} \]

Now the free path is everywhere in combination with one of the coefficients \( A, B, C \) and effect of changed value of \( l \) can be exactly compensated with a change in values of \( A, B, C \).

Jung et al. 2011: \( A = 1.165 \) \( B = 0.480 \) \( C = 1.001 \)
Updated Millikan: \( A = 1.296 \) \( B = 0.435 \) \( C = 0.833 \)
Millikan 1923: \( A = 0.864 \) \( B = 0.29 \) \( C = 1.25 \)

ISO15900

Recommended values for \( S_c, \eta \) and \( l \)

The empirical mobility \( Z \) of a particle depends on its size \( d \) and its electric charge \( q \). The relationship between the electrical mobility and particle size for spherical particle is a function of the slip correction \( S_c \), the dynamic viscosity \( \eta \) and the mean free path \( l \) of gas molecules according to the following equation:

\[ Z = 1 + \frac{2}{d} \left( \frac{A + B \exp \left( \frac{-C}{d} \right)}{3 \pi \eta d} \right) \frac{q}{3 \pi \eta d} \]

Parameter | Value | Remarks
--- | --- | ---
\( S_c \) | 1.962 Air, 1.726 Water | For dry pair at \( \eta = 0.00013 \text{ Pa s} \), \( \nu = 1 \times 10^{-6} \text{ m}^2/\text{s} \)
\( \eta \) | 1.205 K | All values from
\( A \) | 1.296 | J. H. van Deemeter, E.R. Kalousek and D.Y. H. Pawley
\( B \) | 0.435 | J. H. van Deemeter, E.R. Kalousek and D.Y. H. Pawley
\( C \) | 0.833 | J. H. van Deemeter, E.R. Kalousek and D.Y. H. Pawley

A selection of new models


End of the introduction

Proposal and discussion of a new model

New approach

In sake of convenience and accurate interpretation, the new model is made up of the Millikan equation with a diameter complement.

With an aim to take into account the peculiarities of $d < 3$ nm particles; the diameter complement is considered as a function of the particle mass diameter, and when required, of the air temperature and pressure:

$$\Delta d = f(d) \quad \text{or} \quad \Delta d = f(p, T, d).$$

(so far $\Delta d$ was considered as a constant)

Problem: how to determine this function and how to assure simplicity of applications?

Determining of $\Delta d = f(d)$

1. Get a reference table of precise measurements or an exact reference model of $Z = f(d)$. The reference model may have no requirements for simple interpretation and computational.
2. Choose parameters of air $p$, $T$, and a diameter $d$
3. Get the accurate mobility $Z - Z(d)$ from the reference table or compute it by means of the reference model.
4. Calculate by means of plain ISO15900 Millikan model ($\Delta d = 0$) a diameter $d_T$ that corresponds to $Z$ obtained in p.3.
5. Calculate the diameter complement $\Delta d = d_T - d$.

Now the result of plain Millikan equation at $d + \Delta d$ is exactly the same as the reference mobility. We will get different value of $\Delta d$ for every $d$ in the range of $d < 3$ nm and should compile a representative table of function $\Delta d = f(d)$.

Determining of $\Delta d = f(d)$

Next task is: to find a good approximation for the tabulated function $\Delta d = f(d)$. The task is a bit similar to the Cunningham-Millikan problem of looking for approximation the slip correction factor. Unfortunately, we have no physical idea and the search for the approximation is considered as a formal procedure based on intuition and numerical methods of computational mathematics.

A remark: The reference table of measurements of the function $\Delta d = f(d)$ is strongly preferred. Such a table was not available when compiling the presentation and following examples are designed using a reference model.

The reference model

The reference model was based on the $Z = f(d)$ model by Tammet (1995) because the lack of well prepared alternatives. The original model was modified because the approximations of the air viscosity, free path and slip factor coefficients A, B, C should be the same in the Millikan equation and in the reference model. These approximations are prescribed in ISO15900.

Exception: Standard values $B = 0.483, C = 0.997$ may be replaced with recent results $B = 0.480, C = 1.001$.

These changes were entered into the algorithm and the result Tammet95m was used as a tentative reference model.
Experiment 2: Required $\Delta d$

Experiment 3: Fitting of $\Delta d = f(d)$

Experiment 4: Temperature correction

Experiment 5: absolute error of approximation $d = f(Z)$

Experiment 6: relative error of approximation $d = f(Z)$

Experiment 7: pressure error of $d = f(Z)$

Accuracy of approximation $d = f(Z)$

The end of the discussion

Appendixes
Comparison of models

Program A tools, see

http://ael.physic.ut.ee/tammet/A_tools/

Electrical mobility (nm^2 V^-1 s^-1) at 1013 mb and 10 C:

d:nm Millikan Tammem95 Reference Approx T95/Ref Minst/Ref Appr/Ref
0.1 2 0.4682 1.8476 1.9361 0.00759 0.9822 1.5731 0.9458
0.2 1.4449 1.8013 1.4051 1.5619 1.4105 1.0999
0.3 1.1823 1.0543 1.2759 1.0987 1.0985 1.0198
0.4 0.4271 0.5834 0.5648 0.5431 0.5922 1.0586 0.9079
0.5 0.3417 0.3528 0.3199 0.3902 0.9822 1.1976 1.0112
0.6 0.1857 0.1545 0.1570 0.1873 0.9822 1.1823 1.0046
0.7 0.0363 0.0301 0.0343 0.0359 0.9824 0.9224 0.9517
0.8 0.0093 0.0038 0.0036 0.0036 0.9825 0.9567 0.9019
0.9 0.0051 0.0049 0.0049 0.0039 0.9830 0.9019 1.0003
1.0 0.0051 0.0049 0.0049 0.0039 0.9830 0.9019 1.0003

T95 is Tammem (1995) without corrections.

Mkn+ is updated Millikan for d > 0.3 nm.

function E_approx_air (diameter, velocity, d (nm) = real; 
and V (m/s), 1.0959, 1.5940, 4.5986

Excel, inverse function

function E_approx_air (diameter, velocity, d (nm) = real; 
and V (m/s), Excel, how to use?

Excel, how to use?


See and copy the text of one or two macros to the clipboard.

2. Open an Excel worksheet. Choose tools → macro → record new macro → store macro in this workbook → OK. A tiny recorder toolbar will appear. Remember the macro name and press the lower left button. The toolbar disappears and a new empty macro is saved.

3. Choose tools → macro → macros → name of the new macro → edit. VBA window will appear. Select full text of the empty macro and paste the text from the clipboard as a replacement.

4. Go back to the Excel worksheet. Fill three neighbor columns in the worksheet with values of air pressure (mb), temperature (Celsius), and mobility (cm^2 V^-1 s^-1). Write number of rows to be processed into the cell just right of the first value of the mobility (see the example) and click this cell. NB! all data must be presented as values.

5. Choose tools → macro → macros → name of macro → RUN.

References

Fernandez de la Mora, J., de Juan, L., Liedtke, K., Schmidt-Ott, A. (2003) Mass and size determination of nanometer ... 2011) var Viscosity, FlowPath, Xl, X2, y, d; real; real:

begin:
y = 1.6022 * (X1 + X0) * (1 + X0) * (y + y0) - 300 - d;
x1 = [Viscosity + 273.15] / 204.15;
x2 = [Viscosity + 273.15] / 204.15;

visibility wield x = 10 ** d / x * agt(x1) + x2;
FlowPath = 2 * (X1 + X2) /
d;
X0 = A - (underflow safe) then y = 0 else y = exp (-X0 / Kn);
E_approx_air = 1.6022 * (X1 + X0) * (1 + X0) * (y + y0) - 300 - d;
end;

T:C p:mb
record new macro

Sub Z_approx_air() ' HT 20120118 n = ActiveCell.Value For i = 0 To n - 1 mb = ActiveCell.Offset(i, -3).Value Celsius = ... / Kn)Z = 1.6022 * (1 + Kn * (1.165 + 0.48 * y)) / (3 * 3.14159 * vi * dd)ActiveCell.Offset(i, 0) = Z Next i End Sub

http://ael.physic.ut.ee/tammet/A_tools/