CFD in the Capillary Rheometry of Polyethylene Melts

Evan Mitsoulis[1] and Savvas G. Hatzikiriakos[2]
[1]*School of Mining Engineering and Metallurgy, National Technical University of Athens, Zografou, Athens, Greece*
[2]*Department of Chemical and Biological Engineering, The University of British Columbia, Vancouver, BC, Canada*

Keywords: Capillary Rheometery, Polyethylenes, Entrance Pressure, Viscous.

Abstract: The capillary flow of a commercial LDPE melt was studied both experimentally and numerically. The excess pressure drop due to entry (Bagley correction), the compressibility, the effect of pressure and temperature on viscosity on the capillary data analysis have been examined. It was found that only the viscoelastic simulations (using the K-BKZ constitutive relation) were capable of reproducing the experimental data well, while any viscous modeling always underestimates the pressures, especially at the higher apparent shear rates and *L/D* ratios.

1 INTRODUCTION

Capillary rheometry is extensively used in both industry and academia to assess the rheological behaviour of polymer melts at high shear rates (Dealy and Wissbrun, 1990). When such a flow is used and the raw data are collected, a number of important corrections should be applied before the rheological data can be compared with corresponding data from a rotational rheometer (Laun 2003; 2004).

First, capillary flow involves flow through a contraction of a certain angle, known as entrance pressure or Bagley correction [Bagley, 1957]. This pressure is required in order to calculate the true shear stress. Many studies have previously attempted to examine the origin of entrance pressure and its prediction for low-density polyethylenes (LDPEs) (Feigl et al., 1994); (Barakos and Mitsoulis, 1995a); (Beraudo et al., 1996); (Guillet et al., 1996); (Hatzikiriakos and Mitsoulis, 1996; 2003); (Mitsoulis et al., 1998). Only just recently the problem of predicting the Bagley correction for LDPE was solved satisfactorily at extremely high shear rates (up to 1000 s^{-1}) for the first time (Ansari et al., 2010) by taking into account the effect of pressure on the viscosity.

The effect of pressure on the viscosity is very important for some polymer melts, including LDPE. Using capillary data from dies of various length-to-diameter (*L/D*) ratios, the dependence of viscosity on pressure can be assessed (Couch and Binding, 2000); (Park and Dealy, 2006); (Carreras et al., 2006); (Son, 2009); (Aho and Syrjala, 2010); (Koran and Dealy, 1999). As a first approximation, the following Barus equation can be used to determine the parameter, β_p, known as the pressure coefficient of viscosity:

$$\eta = \eta_{p0} \exp\left(\beta_p p\right) \tag{1}$$

where η is the viscosity at pressure *p*, and η_{p0} is the viscosity at ambient pressure. For the LDPE (of main interest in the present work) a value between 1.3×10^{-8} Pa and 4.9×10^{-8} Pa has been reported by various authors (Liang, 2001); (Cardinaels et al., 2007; Park et al., 2008).

The analysis of the dependence of viscosity on pressure is complicated by viscous dissipation (viscous heating) effects. Viscous heating in the capillary extrusion of polymer melts has been the subject of several reviews and studies over the past decades (Winter, 1977); (Ybarra and Eckert, 1980); (Dihn and Armstrong, 1982); (Milthorpe and Tanner, 1987); (Mitsoulis et al., 1988); (Warren, 1988); (Ko and Lodge, 1991); (Rosenbaum and Hatzikiriakos, 1997).

It is the main objective of this work to study the capillary flow of a LDPE melt numerically and experimentally by considering all possible capillary effects, combined and separately. Namely, the effects of Bagley correction, compressibility, pressure dependence of viscosity, and viscous heating will be considered in order to assess the significance of each effect.

Mitsoulis E. and G. Hatzikiriakos S..
CFD in the Capillary Rheometry of Polyethylene Melts.
DOI: 10.5220/0003963602910296
In *Proceedings of the 2nd International Conference on Simulation and Modeling Methodologies, Technologies and Applications* (SIMULTECH-2012), pages 291-296
ISBN: 978-989-8565-20-4

2 EXPERIMETAL

The experimental data used in the present simulations have been obtained for a typical LDPE melt in order to address the effects of pressure, temperature and compressibility on its capillary flow.

The viscoelastic moduli were determined over a wide range of temperatures from 130 to 230°C. Master curves were obtained using the time-temperature superposition principle (TTS), and the results are presented at the reference temperature of 160°C. The polymer was also rheologically characterized in simple extension using the SER-2 Universal Testing Platform from Xpansion Instruments (Sentmanat, 2003).

An Instron capillary rheometer (constant piston speed) was used to determine the entrance pressure (known also as Bagley method) and the viscosity as a function of the wall shear stress, σ_W, and apparent shear rate, $\dot{\gamma}_A = 32Q/\pi D^3$ at 160°C, where Q is the volumetric flow rate and D is the capillary diameter.

3 GOVERNING EQUATIONS

We consider the conservation equations of mass, momentum and energy for weakly compressible fluids under non-isothermal, creeping, steady flow conditions. These are written as (Tanner, 2000); (Mitsoulis and Hatzikiriakos, 2009):

$$\overline{u} \cdot \nabla \rho + \rho \left(\nabla \cdot \overline{u} \right) = 0 \tag{2}$$

$$0 = -\nabla p + \nabla \cdot \overline{\overline{\tau}} \tag{3}$$

$$\rho C_p \overline{u} \cdot \nabla T = k \nabla^2 T + \overline{\overline{\tau}} : \nabla \overline{u} \tag{4}$$

where ρ is the density, $\overline{u}$ is the velocity vector, p is the pressure, $\overline{\overline{\tau}}$ is the extra stress tensor, T is the temperature, C_p is the heat capacity, and k is the thermal conductivity. For a *compressible* fluid, pressure and density are connected as a first approximation through a simple linear thermodynamic equation of state (Mitsoulis and Hatzikiriakos, 2009):

$$\rho = \rho_0 \left(1 + \beta_c p \right) \tag{5}$$

where β_c is the isothermal compressibility with the density to be ρ_0 at a reference pressure p_0 (=0).

To evaluate the role of viscoelasticity in the prediction of Bagley correction, it is instructive to consider first purely viscous models in the simulations. Namely, the Carreau-Yasuda model was used to fit the shear viscosity data of the LDPE melt. The Carreau-Yasuda model is written as:

$$\eta = \eta_{0,C} \left[1 + (\lambda |\dot{\gamma}|)^{\alpha} \right]^{\frac{n_C - 1}{\alpha}} \tag{6}$$

where $\eta_{0,C}$ is the Carreau zero-shear-rate viscosity, λ is a time constant, n_C is the Carreau power-law index, and α is the Yasuda exponent (=2 for the simple Carreau model). The parameters of the model are listed in Table 1.

Table 1: Parameters for *Eq. 6* at 160°C.

Parameter	Value
$\eta_{0,C}$	617,230 Pa·s
λ	17.727 s
n_C	0.221
α	0.215

For the capillary flow simulations the effect of pressure on viscosity can be taken into account by multiplying the constitutive relation with a pressure-shift factor, a_p, defined by the Barus equation, that is (Son, 2009); (Carreras et al., 2006):

$$a_p \equiv \frac{\eta}{\eta_{p0}} = \exp\left(\beta_P p \right) \tag{7}$$

where β_P is the pressure coefficient and p is the absolute pressure, as discussed above.

Viscoelasticity is included using the K-BKZ equation proposed by Papanastasiou et al. (1983) and modified by Luo and Tanner (1988):

$$\boldsymbol{\tau} = \frac{1}{1-\theta} \int_{-\infty}^{t} \sum_{k=1}^{N} \frac{a_k}{\lambda_k} \exp\left(-\frac{t-t'}{\lambda_k} \right) \frac{\alpha}{(\alpha - 3) + \beta I_{C^{-1}} + (1-\beta) I_C} \left[\boldsymbol{C}_t^{-1}(t') + \theta \boldsymbol{C}_t(t') \right] \mathrm{d}t' \tag{8}$$

where λ_k and a_k are the relaxation times and relaxation modulus coefficients, α and β are material constants, and I_C, $I_{C^{-1}}$ are the first invariants of the Cauchy tensor $\boldsymbol{C}_t$ and its inverse $\boldsymbol{C}_t^{-1}$, the Finger strain tensor. Figure 1 plots the master dynamic moduli G' and G'' at 160°C and the model predictions (Kajiwara et al., 1995). The parameters are listed in Table 2.

Table 2: Parameters for the K-BKZ (Eq. 8) at 160°C.

α=7.336			
k	λ_k (s)	a_k (Pa)	β_k
1	1.28×10^{-4}	4.50×10^{5}	1
2	2.51×10^{-3}	98,795	1
3	2.06×10^{-2}	48,899	0.18
4	1.62×10^{-1}	22,089	0.45
5	1.224	8,842	0.049
6	6.733	3,397	0.026
7	43	948.5	0.024
8	248	287	0.014

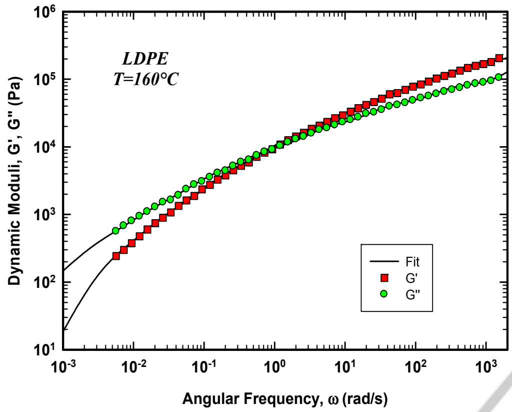

Figure 1: Experimental and model predictions of G' and G'' for the LDPE at 160°C.

Figure 2 plots a number of calculated and experimental material functions for the LDPE melt at the reference temperature of 160°C.

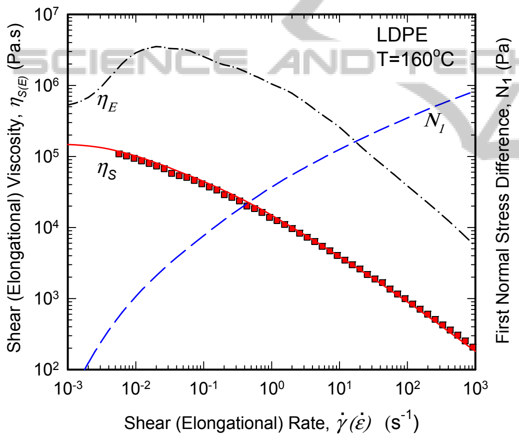

Figure 2: Experimental data (solid symbols) and model predictions of shear viscosity, η_S, first normal stress difference, N_1, and elongational viscosity, η_E, for the LDPE melt at 160°C using the K-BKZ model (*Eq. 12*) with the parameters listed in Table 3.

3.1 Non-isothermal Modeling

For the non-isothermal calculations it is necessary to derive a non-isothermal constitutive equation from the isothermal one. This has done by applying the time-temperature shifting concept as explained by Luo and Tanner (1987; 1988) and will not be presented here. For LDPE melts, the following temperature-shifting function has been found to be adequate for the dependence of rheological properties on temperature (Tanner, 2000); (Meissner, 1975):

$$a_T(T) = \frac{\eta}{\eta_0} = \exp\left[\frac{E}{R_g}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \tag{9}$$

In the above, η_0 is a reference viscosity at T_0, E is the activation energy constant, R_g is the ideal gas constant, and T_0 is a reference temperature (in K). The activation energy constant can be determined from zero-shear-rate viscosity data (Meissner, 1975).

All these properties needed for the non-isothermal simulations are gathered together in Table 3.

4 METHOD OF SOLUTION

The solution to the above conservation and constitutive equations is carried out with two codes, one for viscous flows (*u-v-p-T-h* formulation) and one for viscoelastic flows (Barakos and Mitsoulis, 1996); (Luo and Mitsoulis, 1990). The boundary conditions for the problem can be found in our earlier publications (Mitsoulis et al., 1998); (Mitsoulis and Hatzikiriakos, 2003).

Table 3: Values of the various parameters for the LDPE resin at 160°C.

Parameter	Value
β_c	0.00095 MPa^{-1}
β_p	0.015 MPa^{-1}
m	$0.65\ \mathrm{GPa}^{n_p-1}$ $(0.11\ \mathrm{MPa}^{n_p-1})$
n_p	0.75
ρ	0.7828 g/cm^3
C_p	2.25 J/(g·K)
k	0.0017 J/(s·cm·K)
E	64,100 J/mol
R_g	8.3143 J/(mol·K)
T_0	160°C (433 K)

5 EXPERIMENTAL RESULTS

5.1 Entrance (End) Pressure

Figure 3 plots the entrance pressure (or end pressure due to L/D=0) of LDPE at 160°C as a function of the die length L/D for an extended range of values of the apparent shear rate from 5 s^{-1} to 1000 s^{-1}. This plot is also known as the Bagley plot. The data from an orifice die are also plotted. The data show a curvature with concavity pointing upwards consistent with *Eq. 1* (effect of pressure on viscosity). These results are for a contraction angle 2α=90°.

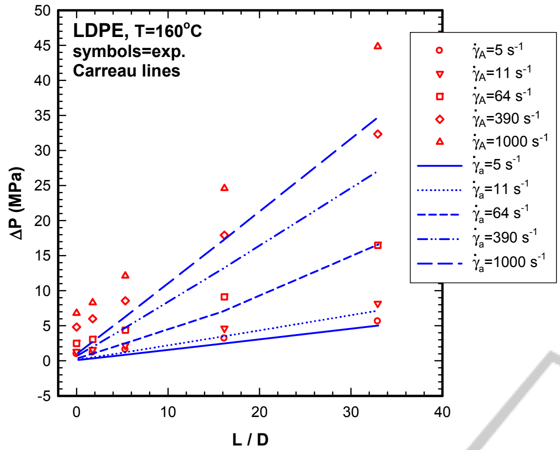

Figure 3: The effect of *L/D* on the pressure for the LDPE melt at 160°C at various values of apparent shear rate (all effects accounted for). Simulations with the Carreau-Yasuda model (*Eq. 6*).

5.2 the Flow Curves

Figure 4a plots the flow curves of LDPE at 160°C obtained with capillary dies having lengths of *L/D*=2, 5, 16, and 33. The Bagley and Rabinowitsch corrections have been applied to the data. Also plotted are the linear viscoelastic data at 160°C, which agree well with the data at *L/D*=2 and 5. The data clearly shows that there is an effect of pressure on viscosity. Using this set of data the β_p (which is a shear-rate-dependent pressure coefficient) can be obtained. In our case, β_p shows a power-law dependency on pressure, according to the following equation:

$$\beta_p = mp^{-n_p} \tag{10}$$

where m=0.62 GPa$^{n_p-1}$ and n_p=0.75, with the pressure p given in GPa. The pressure-corrected data for the LDPE are plotted in Fig. 4b. The data superposes well and the capillary data agrees well with the LVE data.

6 NUMERICAL RESULTS

6.1 Viscous Modeling

It is instructive to perform first calculations with a purely viscous model, so that the effect of viscoelasticity will become evident later. The numerical simulations have been undertaken using the viscous Carreau-Yasuda model (*Eq. 6*). This constitutive relation is solved together with the conservation equations of mass and momentum either for an incompressible or compressible fluid under isothermal or non-isothermal conditions (conservation of energy equation) with or without the effect of pressure-dependence of the viscosity.

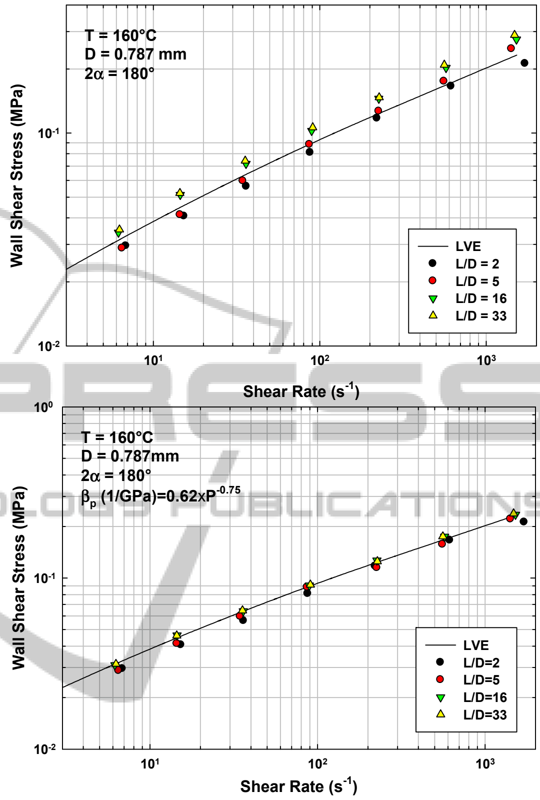

Figure 4: The flow curves of LDPE at 160°C determined in capillary rheometry with dies having *L/D* ratios from 2 to 33. The data at the small *L/Ds* agree well with the LVE data obtained from a rotational rheometer at ambient pressure. The capillary data have been corrected by applying both the Bagley and Rabinowitsch corrections (top) and the effect of pressure on viscosity (bottom).

Collecting all the pressure results together for the 5 dies with *L/D*=0.2, 2, 5, 16, 33 and 5 apparent shear rates $\dot{\gamma}_A$ gives in Fig. 3 the well-known Bagley plot. The experimental results are shown as symbols while the numerical results here and in the subsequent graphs are shown as lines. The results are below the experimental data, and this is mainly due to the inability of a viscous model to capture the end correction (for *L/D*=0). As it was found out in [Ansari et al., 2010], a purely viscous model for LDPE gives end corrections one order of magnitude lower than the experimental ones. It is then at this point that we turn our attention to the viscoelastic results.

6.2 Viscoelastic Modeling

It is again instructive to compare individual distributions of pressure and temperature between the viscous and the viscoelastic models. This is done in Fig. 5, where we show the pressure results from the K-BKZ models for the several pressure drops as in Fig. 3. The viscoelastic pressures are markedly higher than the viscous ones, and in fact they predict the experimental data very well. More detailed simulation results for various cases have shown that the K-BKZ equation is capable of capturing all important effects including the effects of compressibility, pressure, viscous heating and entrance pressure on the overall pressure required in the capillary flow of LDPE.

7 CONCLUSIONS

A commercial low-density polyethylene melt (LDPE) has been studied in entry flows through tapered dies with different *L/D* ratios. The experiments have shown a distinct pressure-dependence of viscosity with a pressure coefficient to be a power-law function of pressure. Full rheological characterization was carried out both with a viscous (Carreau-Yasuda) and a viscoelastic (K-BKZ) model. All necessary material properties data were collected for the simulations.

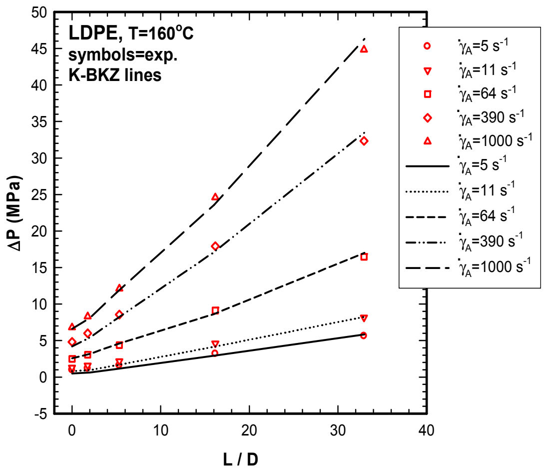

Figure 5: The effect of *L/D* on the pressure for the LDPE melt at 160^{o}C at various values of apparent shear rate. Non-isothermal simulations with the K-BKZ model with pressure-dependence of the viscosity (variable β_p).

The viscous model was found to underestimate the extrusion pressures. The viscoelastic model showed a very good agreement with the experimental results, which appears to be the first in the literature for the elastic LDPE melt. The simulations showed that: (a) compressibility is not important in these steady flows; (b) viscous dissipation is important, especially for the more severe conditions (high *L/D* and apparent shear rates); and (c) the pressure-dependence of viscosity is very important and its correct function has to be found experimentally. This is the first time that all these effects are taken into account in a viscoelastic simulation.

ACKNOWLEDGEMENTS

Financial assistance from the Natural Sciences and Engineering Research Council (NSERC) of Canada and the programme "PEBE 2009-2011" for basic research from NTUA are gratefully acknowledged.

REFERENCES

Aho J., Syrjälä S., *J. App. Polym. Sci.,* 117, 1076-1084 (2010).

Ansari M., A. Alabbas, E. Mitsoulis, S.G. Hatzikiriakos, *Intern. Polym. Proc.,* 25, 287-296 (2010).

Dealy, J. M., Wissbrun, K. F., Melt Rheology and its Role in Plastics Processing - Theory and Applications, *Van Nostrand Reinhold*, New York (1990).

Bagley, E. B., J. Appl. Phys., 28, 193-209 (1957).

Barakos, G., Mitsoulis, E., J. Non-Newtonian Fluid Mech., 62, 55-79 (1996).

Barakos, G., Mitsoulis, E., J. Rheol., 39, 193-209 (1995a).

Barakos, G., Mitsoulis, E., J. Non-Newtonian Fluid Mech., 58, 315-329 (1995b).

Béraudo, C., Coupez, T., Fortin, A., Demay, Y., Vergnes, B., Agassant, J.-F., Proc. XIIth Int. Congr. Rheology, Eds. A. Ait-Kadi, J.M. Dealy, D.F. James, M.C. Williams, Quebec City, Canada, pp. 417-418 (1996).

Cardinaels R., Van Puyvelde P., Moldenaers P., Rheol. Acta, 46, 495-505 (2007).

Carreras, E. S., El Kissi, N., Piau, J.-M., Toussaint, F., Nigen, S., Rheol Acta, 45, 209–222 (2006).

Couch M. A., Binding, D. M., Polymer, 41, 6323-6334 (2000).

Dinh, S. M., Armstrong, R. C., AIChE J., 28, 294-301 (1982).

Feigl, K., Öttinger, H. C., J. Rheol., 38, 847-874 (1994).

Guillet, J., Revenue, P., Béreaux, Y., Clermont, J.-R., Rheol. Acta, 35, 494-50 (1996).

Hatzikiriakos, S.G., Mitsoulis, E., Rheol. Acta, 35, 545-555 (1996).

Laun H. M., Rheol. Acta, 42, 295–308 (2003).

Kajiwara, T., Barakos, G., Mitsoulis, E., *Int. J. Polymer Analysis & Characterization*, 1, 201-215 (1995).

Ko, Y. S., Lodge, A. S., Rheol. Acta, 30, 357-368 (1991).

Koran F., and J. M. Dealy, J. Rheol., 43, 1279-1290 (1999).

Laun H. M., Rheol. Acta., 43, 509-528 (2004).

Liang J.-Z., Polymer, 42, 3709-3712 (2001).

Mitsoulis, E., Hatzikiriakos, S.G., Christodoulou, K., Vlassopoulos, D., Rheol. Acta, 37, 438-448 (1998).

Luo, X.-L., Tanner, R. I., Rheol. Acta, 26, 499-507 (1987).

Luo, X.-L., Tanner, R. I., *Int. J. Num. Meth. Eng.,* 25, 9-22 (1988).

Luo, X.-L., Mitsoulis, E*., Int. J. Num. Meth. Fluids*, 11, 1015-1031 (1990).

Meissner, J., Pure Appl. Chem., 42, 551-612 (1975).

Milthorpe, J. F., Tanner, R. I*., Int. J. Num. Meth. Engng.,* 24, 263-270 (1987).

Mitsoulis, E., Wagner, R., Heng, F. L., *Polym. Eng. Sci.,* 28, 291-310 (1988).

Mitsoulis, E., Hatzikiriakos, S. G., *J. Non-Newtonian Fluid Mech.,* 157, 26-33 (2009).

Mitsoulis, E., Hatzikiriakos, S. G., Rheol. Acta, 42, 309-320 (2003).

Park, H. E., Lim, S. T., Laun, H. M., Dealy, J. M., *Macromolecules*, 47, 1023-1038 (2008).

Park, H. E., Dealy, J. M., *Macromolecules*, 36, 5438-5452 (2006).

Papanastasiou, A. C., Scriven, L. E., Macosco, C. W., J. Rheol., 27, 387-410 (1983).

Rosenbaum, E. E., Hatzikiriakos, S. G., AIChE J., 43, 598-608 (1997).

Sentmanat, M. L., Goodyear Co., U.S. Patent No. 6,578,413 (2003).

Son, Y., J. Polym. Res., 16, 667-671 (2009).

Tanner, R. I., “Engineering Rheology”, 2nd Edition, Oxford University Press, Oxford, UK (2000).

Ybarra, R. M., Eckert, R. E., AIChE J., 26, 751-762 (1980).

Warren, R. C., Viscous Heating. *Rheological Measurement*, Elsevier, London, 119-149 (1988).

Winter, H. H., *Adv. Heat Transfer*, 13, 205-267 (1977).