Review

An assessment of expressions for the apparent thermal conductivity of cellular materials

P. G. COLLISHAW*, J. R. G. EVANS
Department of Materials Technology, Brunel University, Uxbridge, Middlesex, UB8 3PH, UK

Diverse expressions for the thermal conductivity of cellular materials are reviewed. Most expressions address only the conductive contribution to heat transfer; some expressions also consider the radiative contribution. Convection is considered to be negligible for cell diameters less than 4 mm. The predicted results are compared with measured conductivities for materials ranging from fine-pore foams to coarse packaging materials. The dependencies of the predicted conductivities on the material parameters which are most open to intervention are presented graphically for the various models.

Nomenclature

Absorption coefficient	a
Specific heat	C_v ($J\,mol^{-1}\,K^{-1}$)
Emissivity	E
Emissivity of hypothetical thin parallel layer	E_L
Boundary surfaces emissivity	E_0
Fraction of solid normal to heat flow	f
Fraction of total solid in struts of cell	f_s
Mean extinction coefficient	$K\,(m^{-1})$
Effective thermal conductivity of foam	$k\,(W\,m^{-1}\,K^{-1})$
Conductive contribution	$k_{cd}\,(W\,m^{-1}\,K^{-1})$
Convective contribution	$k_{cr}\,(W\,m^{-1}\,K^{-1})$
Thermal conductivity of cell gas	$k_g\,(W\,m^{-1}\,K^{-1})$
Radiative contribution	$k_r\,(W\,m^{-1}\,K^{-1})$
Thermal conductivity of solid	$k_s\,(W\,m^{-1}\,K^{-1})$
Thickness of sample	$L\,(m)$
Diameter of cell	$L_g\,(m)$
Cell-wall thickness	$L_s\,(m)$
Number of cell layers	n
Reflection coefficient	r
Transmission coefficient	t
Absolute temperature	$T\,(K)$
Mean temperature	$T_m\,(K)$
Fraction of energy passing through cell wall	T_N
Temperature of hot plate	$T_1\,(K)$
Temperature of cold plate	$T_2\,(K)$
Volume fraction of gas	V_g
Volume fraction of total solid in the windows	V_w
Refractive index	w
Effective molecular diameter	$\delta\,(m)$
Gas viscosity	$\eta\,(Pa\,s)$
Structural angle with respect to rise direction	θ
Stefan constant	$\sigma\,(W\,m^{-2}\,K^{-4})$

1. Introduction

The sustained interest in low-thermal-conductivity solids emerges from a wide spectrum of needs in refrigeration, cryogenics, packaging of foodstuffs, solar-energy utilization, and the insulation of dwellings, aircraft and submarine cabins. New needs are emerging in the use of high T_c ceramic superconductors. A recent House of Commons Energy Committee report [1] indicates that energy-conservation measures, notably in housing stock, will make significant reductions in UK CO_2 emissions. Restrictions on the use of chlorofluorocarbons as blowing agents have renewed interest in model equations for assessing the loss of thermal resistance brought about the the use of their substitutes.

Most approaches to low-conductivity solids take advantage of the low conductivity of gases and attempt to incorporate a very high volume fraction of the gaseous phase in either a fibrous or a cellular matrix. Developments in porous ceramics take advantage of their facility to evacuate and seal the structure. There is a very large number of expressions relating transport phenomena in two-phase composites to the physical properties of the parent phases, microstructures and volume fractions. Progelhof et al. [2] reviewed some of these expressions and attempted to cover mineral-filled polymers as well as gas-filled cellular materials. Hale [3], in reviewing the physical properties of composites, also dealt, *inter alia*, with thermal conductivity. Taylor [4] reviewed the thermophysical properties of composites and Mottram and Taylor [5] reviewed thermal transport properties in multiphase materials. Crane et al. also reviewed

---

* *Present address:* A B B Transportation Ltd., Derby Carriage Works, Derby, UK

the thermal-conductivity expressions for granular materials [6].

Some expressions are empirical generalizations, while others emerge from detailed consideration of the structure of foams. Some consider only the conductive contribution while others include a term for radiative heat transfer. The convective heat transfer associated with the circulation of gases within a cell is generally ignored and is regarded as insignificant for cell diameters less than 4 mm [3]. Furthermore, most expressions treat the conductivity contributions of the three transport paths as additive thus:

$$k = k_{cd} + k_r + k_{cv} \qquad (1)$$

and while this provides simplicity it detracts from exactitude [7].

Some expressions were developed for other transport processes and are of doubtful applicability to highly porous media. Maxwell's equation [8] for example, was derived for the conductivity of a composite consisting of random spheres distributed in a continuous matrix. Since the spheres should not interact, replacement of the solid by a gas and extrapolation to dispersed phase volume fractions of > 0.9 is of doubtful relevance.

A number of expressions have been developed for porous bodies in which the gas is the continuous phase [9, 10]. Although relevant to unconsolidated powder beds such as sands, no attempt is made here to force these expressions to fit the converse arrangement.

The present work focuses on cellular materials in which an equiaxed gaseous phase is dispersed in a continuous matrix. In fact it has been argued that if the conductivities of the phases differ by a factor of 100 or more the shape of the dispersed phase has little influence on the conductivity of the composite [11]. Since the major phase is gaseous, the apparent conductivity is strongly influenced by the conductivity of the gas. Conductivity of a gas is proportional to the mean free path [12] and hence

$$k_g \propto 1/\delta^2$$

where δ is the effective molecular diameter. Hence many polymeric foams incorporate high-molecular-weight gases such as chlorofluorocarbons. Closed-cell foams are preferred for this reason. Unfortunately, the composition of a gas in the pores of a polymeric foam does not remain constant and there is a steady increase in conductivity as oxygen and nitrogen replace the native gas by permeation under their respective partial pressures. Over a period of several months the conductivity rises [7].

The manufacture of foams with particular characteristics is a difficult task in any event but one of the interesting attributes of a sound predictive model is that it allows the effect of individual variables to be explored in advance of experimental intervention.

2. Expressions for thermal conductivity
2.1. Conductive transfer only
Upper and lower bounds, based on a volumetric law of mixtures, offer the simplest expressions and are cited by several authors [13, 14]. These are obtained by averaging the conductivities and resistivities respectively.

$$k = k_s(1 - V_g) + k_g V_g \qquad (2)$$

and

$$k = \left(\frac{1 - V_g}{k_s} + \frac{V_g}{k_g} \right)^{-1} \qquad (3)$$

The law of mixtures was taken slightly further by Sugawaru and Yoshizawa [15] who introduced an empirical constant, n, which turns out to be 2 or 3 for water or air-saturated firebrick and sandstone. Their expression was validated experimentally in the $V_g < 0.4$ region.

$$k = k_s(1 - A) + k_g A \qquad (4)$$

where

$$A = \frac{2^n}{2^n - 1} \left[1 - \frac{1}{(1 + V_g)^n} \right]$$

The so-called geometric mean is often cited in text books [16] and is based on work by Lees [17] on the thermal conductivity of fabrics

$$k = k_g^{V_g} k_s^{1 - V_g} \qquad (5)$$

Hashin and Shtrikman [18] have presented well-known upper and lower bounds for the magnetic permeability in two-phase composites – these bounds have also been applied to other transport phenomena –

$$k = k_g + \frac{1 - V_g}{\dfrac{1}{k_s - k_g} + \dfrac{V_g}{3k_g}} \qquad (6a)$$

$$k = k_s + \frac{V_g}{\dfrac{1}{k_g - k_s} + \dfrac{1 - V_g}{3k_s}} \qquad (6b)$$

Doherty et al. [19] provided an expression of the form

$$k = \frac{k_g k_s(1 + 2V_g) + 2k_s^2(1 - V_g)}{k_g(1 - V_g) + k_s(2 + V_g)} \qquad (7a)$$

but for low density foams where $V_g \approx 1$, a simplified form is recommended;

$$k = k_g + \tfrac{2}{3}k_s(1 - V_g) \qquad (7b)$$

These expressions also appear in the work of Baxter and Jones [20] and a similar expression appears in Brockhagen [21]. A number of derivations of the thermal or electrical conductivity reduce to Maxwell's equation [8] for polyphase composites in which spheres of one phase are dispersed in a second-phase matrix

$$k = k_s \left[\frac{k_g + 2k_s + 2V_g(k_g - k_s)}{k_g + 2k_s - V_g(k_g - k_s)} \right] \qquad (8)$$

These include Kerner's work [22], the lower bound of Hashin and Shtrikman (Equation 6b), the expression derived by Brailsford and Major [23] – which has been used successfully for particulate filled polymers [24] and was singled out in Hales review [3] and the expression by Hamilton and Crosser [25].

Kuok et al. [26] use Maxwell's relationship, derived for the specific resistance of a dilute suspension of spheres [8], for the thermal conductivity of polyurethane foams. For reasons which are not clear, they

regard the foam as consisting of "random sized spheres of one phase (polyurethane) randomly dispersed in a continuous phase (air)" and rearrange the subscripts and exchange the volume fractions in Maxwell's equation to give

$$k = k_g \left[\frac{2k_g + k_s - 2(1 - V_g)(k_g - k_s)}{2k_g + k_s + (1 - V_g)(k_g - k_s)} \right] \quad (9)$$

Oka and Yamone [27] present an expression for a closed-cell foam. Unfortunately there is a misprint in their equation 17. Using the nomenclature adopted here, their equation 13 reads:

$$\frac{1}{k} = \frac{1}{k_s}(1 - V_g^{1/3}) + \frac{V_g^{1/3}}{k_g V_g^{2/3} + k_s(1 - V_g^{2/3})} \quad (10)$$

Other expressions for mass or electrical transport, and the magnetic permeability or dielectric constant for two-phase materials have been reviewed by Barrer [28] for the diffusion problem in polymer composites. An expression by Bruggeman [29] for particles of various shapes dispersed in a continuous matrix reduces to Equation 11 for the case of spherical particles

$$1 - V_g = \frac{k_g - k}{k_g - k_s}\left(\frac{k_s}{k}\right)^{1/3} \quad (11)$$

Progelhof [30] derived an expression for polymer foams

$$k = k_g \left[1 + \frac{k_s}{k_g}\left(\frac{\rho_a}{\rho_s}\right)^n \right] \quad (12)$$

where ρ_a and ρ_s are the apparent and true densities of the foam and polymer, respectively, and n is an empirical constant.

An expression was derived for the case of ceramic refractory materials by Eucken [31]:

$$k = k_s \frac{1 + 2V_g[(1 - Z)/(2Z + 1)]}{1 - V_g[(1 - Z)/(2Z + 1)]} \quad (13)$$

where $Z = k_s/k_g$.

Russell [32] also derived an expression for porous ceramic insulators which was published in the same period

$$k = k_s \frac{V_g^{2/3} + (k_s/k_g)(1 - V_g^{2/3})}{V_g^{2/3} - V_g + (k_s/k_g)(1 - V_g^{2/3} + V_g)} \quad (14)$$

An expression by Budiansky [33] when applied to a two-phase composite gives

$$\frac{1}{3k} = \frac{1 - V_g}{2k + k_s} + \frac{V_g}{2k + k_g} \quad (15)$$

The model of Jefferson et al. [34] is derived for series and parallel heat flow in a cube containing a particle of the second phase. In principle, therefore, it is limited to $V_g < 0.52$

$$k = k_s \left[1 - \frac{\pi}{4(1 + 2n)^2} \right] + \frac{\pi}{4(1 + 2n)^2}\left[\frac{(0.5 + n)k_a k_s}{0.5k_s + nk_a} \right]$$

where $n = 0.403 \, V_g^{-1/3} - 0.5$ and

$$k_a = k_g k_s \left[\frac{2k_g}{(k_g - k_s)^2} \ln\left(\frac{k_g}{k_s}\right) - \frac{2}{(k_g - k_s)} \right] \quad (16)$$

Topper's series–parallel model for spheres in simple cubic array yields [35];

$$\frac{1}{k} = \frac{1 - 2\phi^{1/3}}{k_s} + \frac{\tan^{-1}\left[\frac{\phi^{1/3}}{(k_s/A - \phi^{2/3})^{1/2}}\right]}{A(k_s/A - \phi^{2/3})^{1/2}} \quad (17)$$

where $\phi = 3V_g/4\pi$ and $A = \pi (k_s - k_g)$. One problem with this model is the condition $k_s/A > \phi^{2/3}$. This means that

$$V_g < 0.75\left(\frac{k_s}{k_s - k_g}\right)^{3/2}$$

so that for a foam with $k_s \simeq 0.21 \, \text{W m}^{-1}\text{K}^{-1}$, filled with air, the maximum permissible condition is $V_g \leq 0.92$.

Much subsequent work has been based on the approach of Tsao [14] who considered the two-phase material to be sectioned, perpendicularly to the direction of heat flow, into layers sufficiently thin that the two-dimensional porosity was constant throughout the thickness. The conductivity was considered to be independent of the stacking order so that it could be deduced from the porosity distribution of layers stacked in ascending order of porosity. The shape of this two-dimensional porosity distribution is needed to evaluate the conductivity.

Considering this distribution to be parabolic, Cheng and Vachon [36] produced an expression which is valid for the case where the dispersed phase has a lower conductivity than the continuous phase

$$\frac{1}{k} = \frac{2}{\{C(k_g - k_s)[k_s + B(k_g - k_s)]\}^{1/2}}$$
$$\times \tan^{-1}\left\{\frac{B}{2}\left[\frac{C(k_g - k_s)}{k_s + B(k_g - k_s)}\right]^{1/2}\right\} + \frac{1 - B}{k_s} \quad (18)$$

where $B = (3V_g/2)^{1/2}$ and $C = -4(2/3V_g)^{1/2}$.

This equation holds for the condition

$$V_g > \frac{2}{3}\left(\frac{k_s}{k_s - k_g}\right)^2$$

so that for a foam with $k_s = 0.21 \, \text{W m}^{-1}\text{K}^{-1}$ filled with air the maximum value of V_g is 0.87.

It is also interesting to see how well an expression deduced for mass transport by diffusion in a two-phase medium can be applied to heat transfer. Bedeaux and Kapral [37] give the following expression which is suitable for large volume fractions of dispersed phase

$$\frac{V_g(k_g - k)}{1 + \frac{(k_g - k)}{3k_s}} + \frac{(1 - V_g)(k_s - k)}{1 + \frac{(k_s - k)}{3k_s}} = 0 \quad (19)$$

Nielsen [38, 39, 40] gives expressions for the elastic moduli of filled polymers which can also be applied to electrical and thermal conductivity [39]. They require two additional parameters related to the viscosity of

the suspensions, but a simplified expression is given in [40] for the elastic modulus of foams in which the volume fraction of occluded gas is high

$$k = \frac{k_s(1 - V_g)}{C} \qquad (20)$$

where $C = 2$–6. Because it presents no dependence on k_g, this expression for modulus does not transpose well for the case of conductivity.

Expressions based on series with ascending powers of V_g have also been devised, for example to express the permittivity of composites [41] but the sensitivity to terms of high powers makes them less applicable as $V_g \rightarrow 1$.

Levy [42] considers the effect of moisture on thermal conductivity and treats the overall conductivity according to a volumetric law of mixtures where the numerical subscript denotes a component of the gas:

$$k = k_s(1 - V_g) + V_{g1}k_{g1} + V_{g2}k_{g2} + V_{g3}k_{g3} \qquad (21)$$

A typical foam can be considered to contain 0.8 atmospheres of blowing agent and 0.2 atmospheres of air and CO_2.

The temperature dependence of the thermal conductivity of foams is studied in detail by Bhattacharjee et al. [43]. Conductivity increases by 0.3–0.5% per degree kelvin in the region 255–422 K. This is a combination of the change in the thermal conductivity of the gaseous phase and the increase in the radiation contribution which is discussed in the next section.

A considerable amount of work deals with the ageing of foams and combines studies of the thermal conductivity, using the model equations described here, in conjunction with studies of the diffusion of gases in foams [44–50]. Typically, increases in conductivity of 30% occur over a period of eight months; the steepest change takes place in the first week.

2.2. Expressions which include a radiation term

Provided the cell size is small enough to limit convection, the deviation between the measured and the predicted conductivity can be attributed to radiative heat transfer. This becomes significant at high-porosity levels [51]. Heat transmitted by radiation expressed as a ratio of heat transmitted by conduction varies with the mean temperature, the sample thickness, the density and the cell size [51]. The radiative contribution to heat transfer as a fraction of the total increases significantly when the foam occludes a low-thermal-conductivity gas. In the search for lower conductivities it can no longer be ignored [52].

The dependence on thickness for still layers of air has been demonstrated experimentally and fits the expression [51]

$$k = k_g + \frac{4\sigma E_0 L T_m^3}{2 - E_0} \qquad (22)$$

provided $290\,K < T_m < 350\,K$.

The dependence on thickness for foams at low thicknesses is strongly influenced by the emissivity of the confining surfaces, but this effect is lost at $L > 15$–$20\,mm$. The total conductivity at infinite sample thickness can therefore be expressed as [51, 19],

$$k(L \rightarrow \infty) = k_c + \frac{4\sigma T_m^3 E L_g}{2 - E} \qquad (23)$$

Since L_g is strictly the thickness of the layers of static air, it is increased by increasing the cell sizes and it is decreased by increasing the foam density.

Glicksman et al. [53] developed an expression using the mean extinction coefficient of the foam, which can be measured directly to an accuracy of 10% by infrared spectroscopy. If the foam sample is greater than 6 mm thick, radiant heat transfer can be considered as a diffusion process, and the flux can be treated as a sum of conductive and radiative terms

$$q = -k_c \frac{dT}{dx} - \frac{16\sigma T_m^3}{3K} \frac{dT}{dx} \qquad (24)$$

Schuetz and Glicksman [54] assessed that the proportion of polymer in the walls is 10–20%, with the remainder in the struts, and gave equations for the thermal conductivity of gas mixtures. An expression for the conductive term was then developed by considering a cubical arrangement of cells giving an upper limit

$$k = k_g + (\tfrac{2}{3} - \tfrac{1}{3} f_s)(1 - V_g)k_s \qquad (25a)$$

and a lower limit

$$k = k_g + 0.8(\tfrac{2}{3} - \tfrac{1}{3} f_s)(1 - V_g)k_s \qquad (25b)$$

In addition, the radiative term is

$$k_r = \frac{16\sigma T_m^3}{3K} \qquad (25c)$$

The mean extinction coefficient, K, is measured on slices of foam of varying thickness using an infrared spectrophotometer and averaging the transmission I/I_0, in the 5–30 μm wavelength region from which

$$\frac{I}{I_0} = c \exp(-KL) \qquad (26)$$

Values of the mean extinction coefficients for foam were in the region 1400–2500 m^{-1}. The model for the radiation contribution is refined further by considering the transmission of radiation by the windows and struts [55]. The same expression for the conduction is retained. The cell walls are considered to be 90% transparent to infrared radiation while the struts are opaque. The cells are treated as pentagonal dodecahedra and the struts are inscribed within equilateral triangles. The mean extinction coefficient is proportional to the total surface area of the struts per unit volume of foam. This is proportional to the square root of the foam density and inversely proportional to the cell diameter. This gives two terms for the radiation transfer:

$$k_r = \frac{16\sigma T_m^3}{3} \left[\frac{4.1\,(f_s \rho_r/\rho_s)^{1/2}}{L_g} + \frac{(1 - f_s)\rho_r}{\rho_s} K \right]^{-1} \qquad (27)$$

Here K is the wavelength-averaged extinction coefficient of the solid polymer. Values of K in the range

$6\text{-}16 \times 10^4 \, \text{m}^{-1}$ were used for polyurethane. The subscripts to the density, ρ, refer to foam and solid polymer.

Boetes and Hoogendoorn [52] arrived at an expression which includes the fractions of radiation transmitted through or reflected from the cell walls t and r, respectively and the boundary emissivity, E_0

$$k = k_c + \frac{4\sigma L \, T_m^3}{\dfrac{L}{L_g}\left(\dfrac{2}{1-r+t} - 1\right) + \dfrac{2}{E_0} - 1} \quad (28)$$

For their polyurethane foams, values of $r = 0.0335$ and $t = 0.758$ were derived. For k_c they used the cubical strut model of Schuetz and Glicksman [54]

$$k_c = k_g + (\tfrac{2}{3} - \tfrac{1}{3}f_s)(1 - V_g)k_s$$

and since $f_s \sim 0.8$

$$k_c = k_g + 0.4(1 - V_g)k_s \quad (29)$$

Cunningham [56] also approached the problem from a simplified structural model in which 80% of the polymer is incorporated in the struts and 20% in the windows. The value of k_g for blowing agent R11 diluted with CO_2 was taken as $0.008 \, \text{W m}^{-1}\text{K}^{-1}$ at 283 K. Boetes and Hoogendoorn [52] used $0.009 \, \text{W m}^{-1}\text{K}^{-1}$ at 195 K. Radiative contributions to the total experimental conductivity were at least 30%, in good agreement with Boetes' value of 26%. Cunningham discussed radiation in terms of Equation 22 but showed that this gives a k_r value which is too low if L is put equal to L_g, as in Equation 23. An upper bound for k_r is obtained by putting $L = NL_g$, where N is the average number of cells traversed by the radiation before it is absorbed by a strut. Putting $N = 4$ offers a slightly better fit to the values of k_r deduced from the measured k and the calculated k_c, but further deviations occur as the value of f_s falls at low cell sizes as a result of window transparency and emissivity. Radiative contributions to the conductivity of polyurethane foams are in the region $0.006 \, \text{W m}^{-1}\text{K}^{-1}$ [56].

Equations for the conductive transport in the direction parallel to the rise direction, k_{II}, and the transverse direction, k_I are given as

$$k_{II} = k_g + (\cos^2 \theta)(1 - V_g)k_s$$
$$\quad + (\sin^2 \theta)(1 - f_s)(1 - V_g)k_s \quad (30a)$$
$$k_I = k_g + 0.5\sin^2\theta(1 - V_g)k_s$$
$$\quad + 0.5(\cos^2\theta + 1)(1 - f_s)(1 - V_g)k_s \quad (30b)$$

A typical value of θ is $40°$ [7]. Williams and Aldao [57] also give k_r/k as 7–30% depending on the sample thickness and cell size. In their experiments the dependence of k_r on the sample thickness is stable for $L > 10 \, \text{mm}$. Their model considers reflection and transmission of radiation through a stack of parallel layers perpendicular to the direction of heat flow and yields

$$k = k_g + \frac{4\sigma T_m^3 L}{1 + (L/L_g)(1/T_N - 1)} \quad (31)$$

T_N is the net fraction of radiant energy sent forward by a solid membrane, while $(1 - T_N)$ is sent back by reflections from both surfaces of the solid layer

$$T_N = \frac{(1-r)}{(1-rt)}\left[\frac{(1-r)t}{(1+rt)} + \frac{(1-t)}{2}\right] \quad (32)$$

The fraction r represents the incident energy sent back at each interface and is given by [58]:

$$r = \left(\frac{w-1}{w+1}\right)^2 \quad (33)$$

Upper and lower values of T_N for polymers, deduced from the range of refractive indices available and from the limiting values of t of 0 and 1, produce $0.466 < T_N < 0.959$. The radiative contribution, k_r, is very sensitive to T_N in the region $0.8 < T_N < 0.959$, suggesting that fillers or pigments, by increasing absorption, will decrease T_N.

Valenzuela and Glicksman [7] use a radiation term as follows

$$k_r = 4\sigma F T_m^3 L_g \quad (34)$$

where F is a shape factor which also includes the emmisivity of the polymer. Thus for $E = 1$ and for a cubic cell model in which the side walls are at the mean temperature, $F = 0.6$. In fact, Doherty et al. [19] suggested that for polyurethanes $E = 0.85$. This radiation model represents an upper bound, and assumes that the walls are opaque. If the walls are transparent, equation 34 underestimates k_r [59]. It uses the Doherty et al. equation (Equation 7a) for the conductive contribution, k_c.

Loeb [59] presents a model which incorporates the radiative transfer but requires the structural parameters P_c (the fraction of the cross-sectional area perpendicular to the direction of heat flow occupied by pores) and P_L (the fraction of length occupied by pores in the direction of heat flow) whereupon

$$k = k_s\left\{1 - P_c\left[\frac{P_L(1-R)}{P_L(1-R) + R}\right]\right\} \quad (35)$$

where $R = 4\gamma\sigma E L_g T_m^3/k_s$ and γ is a shape factor ($\gamma = 2/3$ for spherical pores). Using similar nomenclature, Francl and Kingery [60] presented the following expression which incorporates radiative heat flow

$$k = k_s\left(1 - P_c + \frac{P_c}{P_L/R + 1 - P_L}\right) \quad (36)$$

Batty et al. [61] have developed Tsao's model [14] by assuming that the curve enclosing the solid phase can be represented by the function $y = a \, \text{cosech} \, x$, so that the conductivity can be directly calculated from a knowledge of void volume fraction. This model does not have the upper limits associated with Equation 18 in Section 2.1.

In order to use the model it is necessary to find the parameter a from the value of V_g. This is given by

$$1 - V_g = a[\ln \tanh \tfrac{1}{2} - \ln \tanh (\tfrac{1}{2}\sinh^{-1} a)]$$
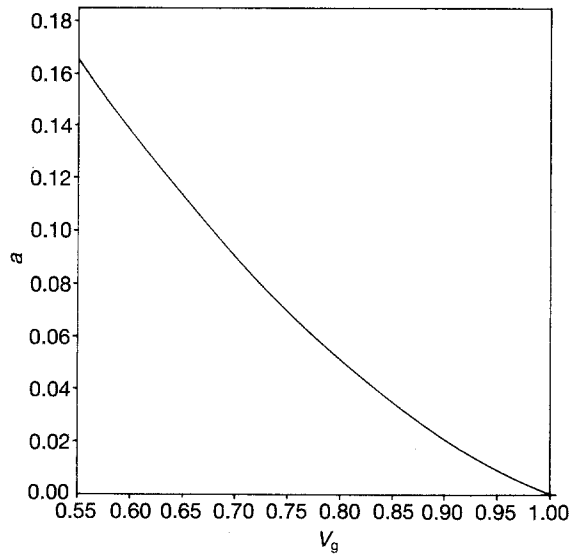$$\quad + \sinh^{-1} a \quad (37)$$

and is plotted in Fig. 1.

Figure 1 The dimensionless parameter a, deduced from Equation 37 for use in Equation 38 for the conductive contribution to the thermal conductivity of foams.

where the cube of the mean temperature is given by

$$T_m^3 = (T_1^2 + T_2^2)(T_1 + T_2)/4 \qquad (42)$$

which differs slightly from the cube of the arithmetic mean. Thus a plot of the apparent thermal conductivity as a function of T_m^3 gives a straight line and the mean extinction coefficient, K, can be calculated from its gradient. The expression is valid for large optical thicknesses, and for isotropic scattering, and it has been applied to the heat transfer in ceramic aerogels [64]. These materials present some Rayleigh scattering in the visible region, but not in the infrared, where extinction is solely due to absorption [65]. They are also capable of evacuation, so that the gas conductivity and its temperature dependence do not contribute to the apparent conductivity. However, they do have low absorption in the 3–7 μm wavelength region; this is discussed below.

Linear-anisotropic-scattering models have been developed to account for the radiative component of heat transfer in fibrous insulators [66, 67].

The conductive contribution is given by

$$k_c = \left[\frac{\sinh^{-1} a}{k_s} + \left\{ \frac{a k_s}{\cosh 1 - \cosh(\sinh^{-1} a)} \right. \right.$$

$$\left. \left. + \frac{k_g}{1 - \sinh^{-1} a + \frac{a}{(1 + a^2)^{1/2}} \ln \left[\frac{[e - \exp(\sinh^{-1} a)] - a - (1 + a^2)^{1/2}}{[e - \exp(\sinh^{-1} a)] - a + (1 + a^2)^{1/2}} \right] } \right\}^{-1} \right]^{-1} \qquad (38)$$

The radiative term is given by

$$k_r = \frac{4\sigma L T_m^3}{\left[\frac{2}{E_0} - \frac{L}{L_g} + \frac{2(L - L_g)}{EL_g} \right]} \qquad (39)$$

Harding [62] gives an empirical expression for the conductivity of polyurethanes as

$$k = k_s E_s(1 - V_g) + k_a V_g + (k_b - k_a)V_g$$

$$\times (1 - F_i)(1 - 0.5R_g V^{1/3})^m$$

$$+ \frac{C_r V^{1/3}}{V_g} \left(\frac{T_1 + T_2 + 920^3}{1000} \right) \qquad (40)$$

Where E_s is a constant which is approximately equal to 0.74, k_a is the thermal conductivity of air and k_b is that of the blowing agent, F_i is the volume fraction of interconnected pores, approximately equal to 0.02, V is the absolute volume of gas in an average cell, approximately equal to 3×10^{-10} m^3, m is the molar fraction of the blowing agent, C_r is a radiative coefficient, T_1 and T_2 are the hot and cold wall temperatures, and R_g is the ratio of cut surface per unit volume.

For high-temperature porous insulation materials the radiation term is given by [63]

$$k_r = \frac{16w^2 \sigma T_m^3}{3K} \qquad (41)$$

2.3. Convective heat transport

The contribution to conductivity by convection is discussed by Valenzuela and Glicksman [7]. The cell diameter below which convection should be negligible is variously quoted in the range 3–10 mm. The experimental results of Skochdopole [68] show that a 4 mm diameter is the limit for air-filled foams. The corresponding limit for chlorofluorocarbon-filled foams is therefore likely to be in the 1.5 mm diameter region.

Progelhof et al. [2] argue that the convective heat transfer in a foam should be proportional to the cell diameter raised to the fourth power, as well as to the properties of the gas. They also point out that convective transport is anisotropic in foams which have a pronounced structural rise direction.

Jeffreys [69] showed that the onset of convective flow in a layer of fluid of thickness L_g, coefficient of expansion α, kinematic viscosity ν and thermal diffusivity κ will occur when the dimensionless parameter λ, given by:

$$\lambda = \frac{9.81 \, \alpha(T_1 - T_2)L_g^3}{\kappa \nu} > 1709.5 \qquad (43)$$

where T_1 and T_2 are the temperatures at the boundaries. Calculated values for typical foams with 1 mm pores give values of λ four orders of magnitude lower than this.

3. Values of the conduction and radiation parameters for typical insulation materials

The conductivity of solid polyurethane is generally taken as $0.250 \, W \, m^{-1} \, K^{-1}$ after Cunningham [56] and Schuetz and Glicksman [54]. Cunningham comments on the wide variability of this value in the literature. Thus, Norton [46] quotes $0.167 \, W \, m^{-1} \, K^{-1}$ while Healy [70] gives $0.348 \, W \, m^{-1} \, K^{-1}$. The value for solid polyimide is taken as $0.290 \, W \, m^{-1} \, K^{-1}$ [71] and is $0.330 \, W \, m^{-1} \, K^{-1}$ [2] for polyethylene.

For the ceramic aerogels, which can have voidage up to 99%, pores are in the 1–100 nm region, and the solid phase consists of bridged particles a few nanometres in diameter. The solid-phase conductivity contribution in silica aerogels can be as low as $10^{-3} \, W \, m^{-1} \, K^{-1}$, and correcting to full density gives a solid-phase conductivity less than that for silica glass [72]. The solid conductivity must then be deduced from the apparent-conductivity–temperature plots. The solid conductivity, k_s, varies with $\rho_f^{0.9}$ for translucent aerogels.

Gas-phase conductivities are $0.0263 \, W \, m^{-1} \, K^{-1}$ for air at 20 °C [73], but for traditional polyurethane foams a mixture of gases fill the pore space. Valenzuela and Glicksman [7] take the thermal conductivity of a chlorofluorocarbon blowing agent as $0.0082 \, W \, m^{-1} \, K^{-1}$ at 0 °C in the fresh foam, and consider it to rise to $0.0143 \, W \, m^{-1} \, K^{-1}$ when the diffusion of air has occurred and the molar fraction of air is 0.7. In order to calculate the conductivity of the gas mixture they applied an expression derived by Wilke [74]

$$k_g = \frac{x_1 k_1}{x_1 + x_2 A_1} + \frac{x_2 k_2}{x_2 + x_1 A_2}$$

where
$$A_1 = \frac{1 + (k_1/k_2)^{1/2}(m_2/m_1)^{1/4}}{(8 + 8m_1/m_2)^{1/2}}$$

and
$$A_2 = \frac{1 + (k_2/k_1)^{1/2}(m_1/m_2)^{1/4}}{(8 + 8m_2/m_1)^{1/2}} \qquad (44)$$

In fact, this is an expression for the viscosity of a mixture of gases with the viscosities replaced by the conductivities. The justification for this seems to emerge from the ratio $kM/\eta C_v$, which is theoretically equal to unity, but lies between 1.4 and 2.5 for a range of gases [75].

Cunningham et al. [56] discussed the effect of the CO_2 produced during reaction on the conductivity of the gaseous phase. Taking the conductivity of the blowing agent, R11, as $0.007 \, W \, m^{-1} \, K^{-1}$ and of the CO_2 as $0.015 \, W \, m^{-1} \, K^{-1}$, it was estimated that 25% of the CO_2 by volume increased the cell gas conductivity to $0.008 \, W \, m^{-1} \, K^{-1}$. The diffusion of air during ageing and the solution of the blowing agent in the polymer have a more serious effect in increasing k_g.

Norton [46] suggested that the molar rule of mixtures for thermal resistance best predicts the thermal conductivity of gas mixtures, thus,

$$1/k_g = x_1/k_1 + x_2/k_2 \qquad (45)$$

and several sources of experimental data were cited which fit this relationship. Batty et al. [61] used this

formula with an estimated volume fraction (molar fraction) of fluorocarbon of 0.4, the remainder being air, to give $k_g = 0.014 \, W \, m^{-1} \, K^{-1}$. Since this value agrees with others [7] it was used in the present calculations.

For ceramic aerogels with pore sizes in the 1–100 nm region, the bulk-gas-phase conductivity is not attained even when the pore gas pressure is 1 atmosphere [76]. Under fine-pore conditions, the gas conductivity is related to the conductivity at ambient pressure in the bulk ($K_n = 0$), k_{go} and the Knudsen number $K_n = \bar{l}/L_g$ by

$$k_g = k_{go}/(1 + 2\beta K_n) \qquad (46)$$

where $\bar{l}$ is the mean free path, L_g is the pore diameter and β is 1.5 for air.

The extinction coefficients of individual foams can be obtained from the experimental relationship between K and the foam density obtained by Schuetz and Glicksman [54] for polyurethanes. In Equation 27, K is the mean extinction coefficient for the solid polymer and values in the range 6–$16 \times 10^4 \, m^{-1}$ are quoted for polyurethane [55].

A problem with the wavelength dependence of the extinction coefficient occurs with ceramic aerogels. These are generally transparent in the visible region but strongly absorbing in the infrared, making them ideal in solar-energy applications [77]. Because of their open-cell structure they can be evacuated and sealed to give minimum leakage, whereupon apparent conductivities down to $2 \, mW \, m^{-1} \, K^{-1}$ can be obtained. This compares with $11 \, mW \, m^{-1} \, K^{-1}$ for a ClF_2-filled gel and $19 \, mW \, m^{-1} \, K^{-1}$ for the aerogel [65]. In fact, the apparent conductivity only rises significantly at 0.1 atmosphere [72]. However, they present a window of transparency in the 3–7 μm region and attempts have been made to select opacifiers with high absorption in this region but which retain transparency in the visible [77]. Some progress has been made with opacifiers based on oxides of iron [76, 78]. Adsorbed water also increases absorption in this band [76].

Equations derived for polymer foams also incorporate structural parameters. The fraction of total solids in the struts was taken as 0.8 after Cunningham [56]. Cunningham [56] has commented that Equation 23 underestimates the radiative contribution and that L_g should be replaced by $4L_g$ – the approximate distance over which radiation is absorbed. This factor was incorporated in the calculations for Equation 23.

For the emissivity of polymer layers, Jones [51] took 0.68 while Cunningham [56] suggests a minimum value of 0.5. Doherty et al. suggest $E = 0.85$ [19] and Batty et al. suggest 0.8 [61]. The last value was used here. The emissivity of the confining surfaces was taken as 0.9. Reflectivities of polymers, based on the range of refractive indices, lie between 0.02 and 0.07 [57] and 0.034 [52] is the value used here for polyurethanes. Similarly, the transmission coefficient was taken as 0.49 for polyurethane [52] and as 0.57 for polyethylene [79].

In the calculations which follow, the density of solid polyurethane was taken as $1150 \, kg \, m^{-3}$ [80]; this is

the value used by Kuok *et al.* [26]. Norton [46] quotes $1240 \, \text{kg m}^{-3}$. The density of solid polyimide was deduced from data in [81] as $1340 \, \text{kg m}^{-3}$.

4. Assessment of apparent-conductivity expressions

Assessment of the expressions was made by reference to a series of polyurethane foams covering a range of densities, a very-low-density polyimide foam and a sample of large-cell polyethylene packaging.

Polyurethane foam samples were supplied by Baxenden Chemicals of Accrington, Lancashire, UK in October 1990, along with conductivity data obtained, according to ASTM C-518, at a 24 °C mean temperature.

A sample of a polyimide foam (trade-name Solimide) was supplied by Dowty Energy Control Products of Ross on Wye, Hereford, UK. Its thermal conductivity measured at 24 °C is also shown in Table I. A sample of polyethylene blister packaging (grade L70) was supplied by Jiffy Packaging Company Ltd of Winsford, Cheshire, UK. All the materials were obtained in September or October 1990.

The guarded hotplate method [82] was used to determine the thermal conductivity of stacks of blister packaging. Type-K thermocouples which had been calibrated against a mercury-in-glass thermometer with a BSI (British Standards Institute) certificate were used for measurement of the surface temperatures.

Foam samples were fractured after immersion in liquid N_2 and examined by scanning electron microscopy (SEM) using a Cambridge Stereoscan S250 to obtain the average cell diameter and cell-wall thickness. Image analysis was performed using a VIDS four-dot-measurement software package on an Apple II microcomputer. In foams which showed some elongation in the rise direction, the anisotropy was ignored and the average was calculated from equal populations in both directions. Thus, any distortion of cells during fracture would not change L_g significantly. Cell-wall-thickness measurements were taken from walls oriented parallel to the beam, but these values were not used in the calculations. The results are shown in Table I.

The density of the foams were individually measured (Table I). The boundary emissivity was taken as

0.9 [52]. In the calculations, sample thickness has little influence on k_r when $L \gg L_g$, and it was taken as 50 mm throughout.

The mean temperature, T_m, was taken as 297 K to correspond to the measurements for the foams. It was taken as 315 K for the polyethylene. Samples RM500 and RM520 are chloroflorocarbon-free, but no adjustment to the gas conductivity for partially aged foams was made. Even for a CO_2-filled foam, the gas-phase conductivity is close to the value of $0.014 \, \text{W m}^{-1} \text{K}^{-1}$ used in the calculations.

5. Calculation of conductivity contributions

Fig. 2 shows the fracture surface (fractured after chilling in liquid nitrogen) for the polyimide foam of voidage 99.5%. It shows two cells which have been opened by the fracture and one which remains sealed. The arrangement of the struts is clearly seen, and it supports the general view that approximately 80% of the material is contained in the struts.

Fig. 3 shows the experimental data points for the polyurethane foams together with the predictions of many model expressions for conductivity using the polyurethane properties. Some of the conductivity equations are not plotted here. Equations 16–18 are omitted because they are invalid for the range of V_g involved. Equation 20 is omitted because it gives $k < k_g$. At first sight some of the equations show a remarkably good fit, notably Equations 11 and 38. The fit for Equation 12 arises from the arbitrary selection of $n = 1.3$. It should be remembered that these are expressions for the conductivity term only, and it is variously argued that radiation contributes 20–30% to the overall conductivity of foams [57, 52]. What is especially interesting about the results is that Equation 38, deduced from a detailed mathematical treatment of the structural geometry of a foam, provides a remarkably good prediction of the conductivity. If radiative contributions are to be added, the equations showing the best fit to the data are Equations 11, 38, 25, 30b and 4 ($n = 2$).

Considering the conductivity contribution first, the effect of individual parameters can now be deduced. Fig. 3 shows the ability of the expressions to account for the effect of the volume fraction of the dispersed phase (gas). Fig. 4, on the other hand, shows the effect

TABLE I Physical properties of cellular materials

Material	Grade	Foam density (kg m^{-3})	k(measured) $(\text{W m}^{-1} \text{K}^{-1})$	L_s (μm)	L_g (μm)	K (m^{-1})	$V_g{}^a$	a
Polyurethane	RM126	31	0.018	0.4	320	1430	0.973	0.004
Polyurethane	RM130	50	0.020	0.4	410	2200	0.957	0.007
Polyurethane	DP8436	80	0.022	1.2	220	3360	0.930	0.013
Polyurethane	PE406W	96	0.028	5.6	330	3950	0.917	0.0165
Polyurethane	RM500	173	0.032	8.0	340	6720	0.850	0.035
Polyurethane	RM520	234	0.036	3.6	240	8820	0.797	0.051
Polyimide	Solimide	7	0.042	7.5	402	374^b	0.995	0.001
Polyethylene	L70	9	0.099	35	25000	-	0.990	0.001

^{a} Correction for cell gas density at 0.7 molar fraction of air gives a maximum error of 0.001 in V_g for RM126 and was thus ignored.
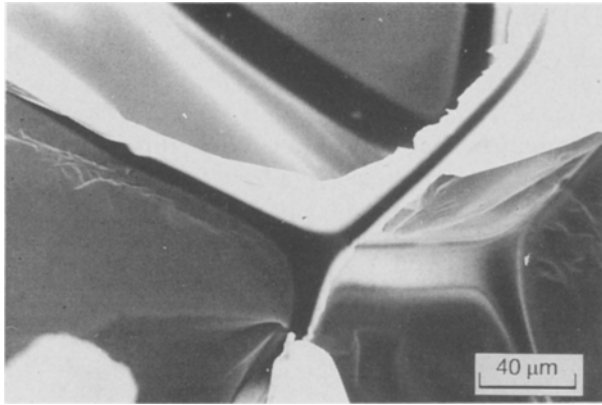^{b} Based on experimental data for polyurethane foams [54].

Figure 2 The structure of the polyimide foam (99.5% voidage) fractured after chilling in liquid nitrogen. The arrangement of the struts can be seen clearly.

of the conductivity of the solid phase for an air filled foam ($k_g = 0.0263 \, \mathrm{W \, m^{-1} \, K^{-1}}$) of voidage 0.9. This graph uses logarithmic axes to accommodate the range of materials. The selected equations from Fig. 3 fall in a narrow band giving predictions for polymer, mineral-filled polymer, ceramic and metallic foams.

Fig. 5 shows the effect of the conductivity of a gas for a foam with $V_g = 0.9$ and $k_s = 0.25 \, \mathrm{W \, m^{-1} \, K^{-1}}$. These relationships are nearly linear with gradients close to unity so that the effect of the gas conductivity can be crudely described in the form

$$k \;=\; k_g + C$$

In fact, the gradients for the equations used in Fig. 5 vary from 0.96 to 1.05 and the intercept, C, varies from $0.008 \, \mathrm{W \, m^{-1} \, K^{-1}}$ to $0.011 \, \mathrm{W \, m^{-1} \, K^{-1}}$, but to a first approximation the effect of changes to the cell gas can be crudely estimated if the dependence of C on the void volume is known at high values of V_g. The constant C can be regarded as the notional contribution to conductivity of a foam of 10 vol % solids when the conductivity of the gas and radiative contributions are zero. In this case, it represents 3.2–4.4% of k_s for the different equations used in Fig. 5. Fig. 6 uses the sophisticated equation of Batty *et al.* [61], Equation 38, to see the dependence of k/k_s at $k_g = 0$ as a function of V_g. Multiplying the ordinate by k_s and adding k_g gives an estimate of the conductivity of polyurethane foams which differs from the value in Equation 38 by 4% at $V_g = 0.85$ and by less than this at $V_g > 0.85$.
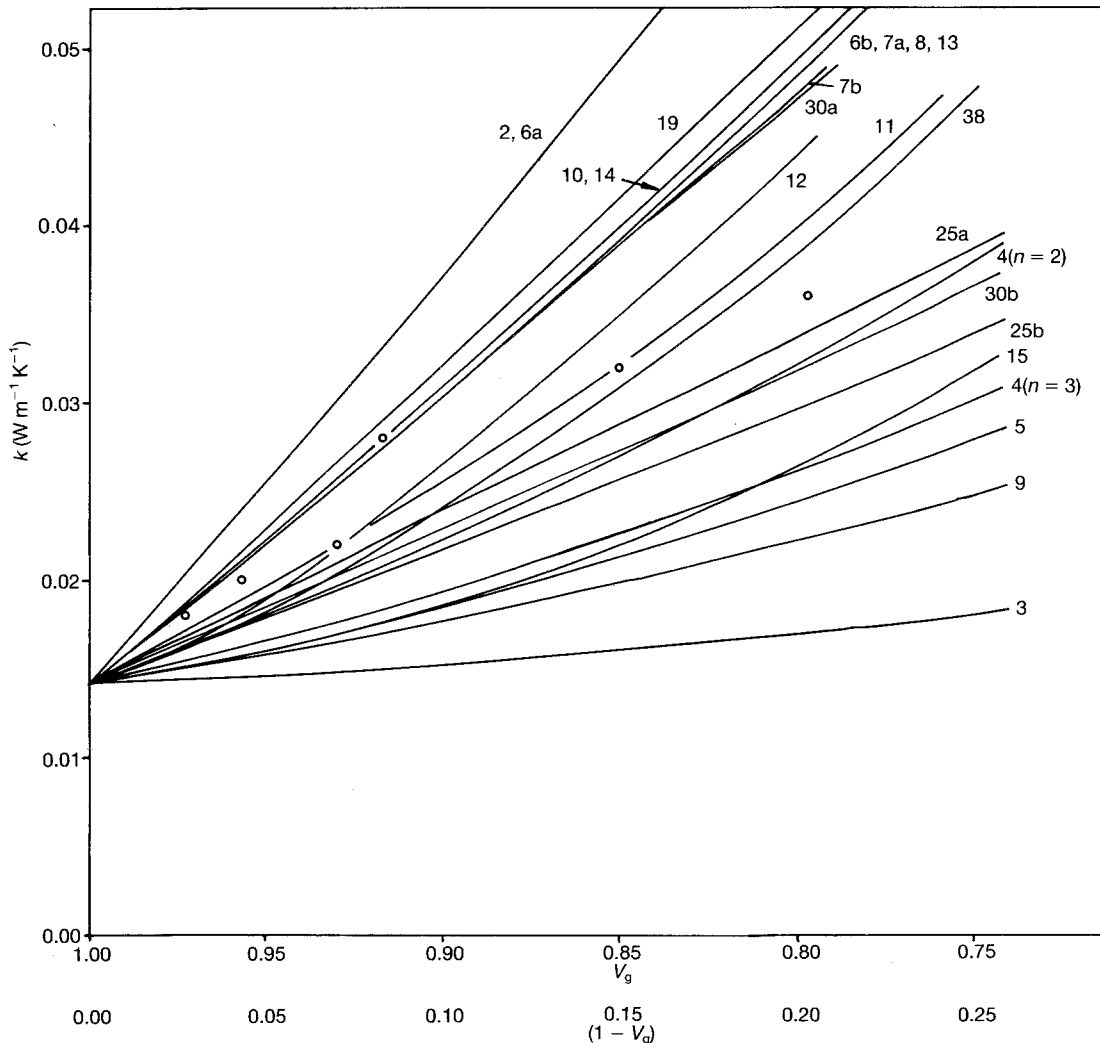

Figure 3 The data points for the thermal conductivity of commercial polyurethane foams of various densities superimposed on plots for diverse expressions for the conductivity of polyurethane foams. The curves are labelled with equation numbers from the text.
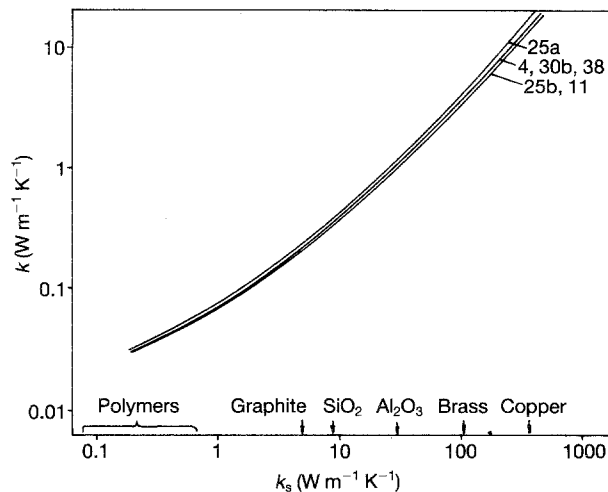
Figure 4 The effect of the conductivity of the continuous (solid) phase on the thermal conductivity of an air-filled ($k_g = 0.0263 \text{ W m}^{-1}\text{ K}^{-1}$) foam of voidage 0.9. The band encloses plots for Equations 4 ($n = 2$), 11, 25, 30b and 38.
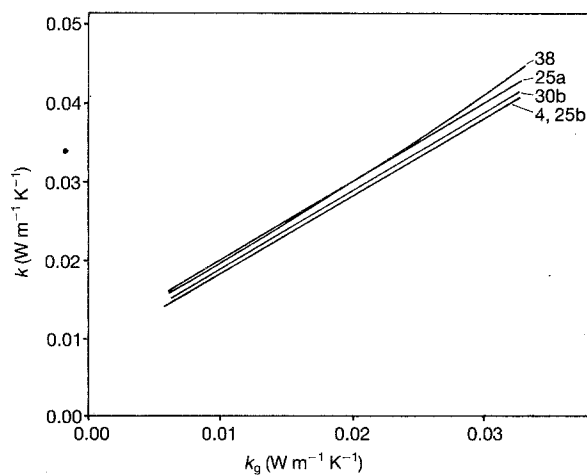

Figure 5 The effect of the conductivity of the cell gas on the apparent conductivity of a polyurethane foam of voidage 0.9 with $k_s = 0.25 \text{ W m}^{-1}\text{ K}^{-1}$. The curves are labelled with equation numbers from the text.
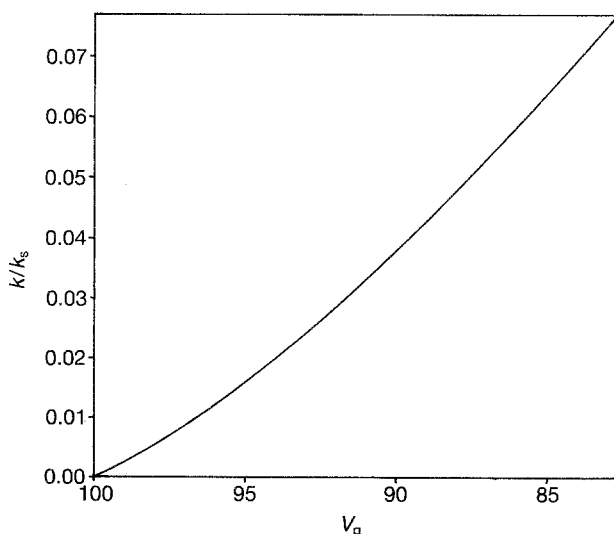

Figure 6 Apparent conductivity, k, as a fraction of the conductivity of the solid phase k_s, for the notional condition $k_g = 0$, expressed as a function of the voidage, V_g, using Equation 38.

6. Calculation of radiation contributions

The contributions from radiation are shown in Table II. Equation 34 is sensitive only to the cell diameter, and rounding produces $k_r = 0.001$ for all the polyurethane foams. Equation 39 also predicts a low value of k_r for all the polyurethane foams, so that the radiative contribution is only 3–6% of the measured conductivity. Averaging the other predictions (the penultimate column of Table II) shows a systematic decrease in the radiative contribution as the polyurethane-foam density increases. This is mainly the influence of Equations 25 and 27 which include the extinction coefficient and foam density as variables. When the radiative contribution is expressed as a percentage of the measured conductivity (the last column of Table II) the importance of the radiative contribution in foams of very low density is emphasized.

All the expressions for radiative contributions in-corporate the cube of the mean absolute temperature and the calculations in Table II employ $T_m = 297 \text{ K}$. It follows that, for cryogenic applications, radiation is less important, but it becomes more influential at higher absolute temperatures; this effect is well-known in refractory technology.

Equations 28 and 31 show a strong dependence of the radiative contribution on the transmission coefficient and this sensitivity is shown in Fig. 7 for the full range of transmission coefficient, and for the characteristics of polyurethane foam DP8436, which is of intermediate density. Such a dependence suggests interventions such as the addition of fillers to reduce the transmission. A similar approach has been taken in the case of ceramic aerogels [76–78]. In polymers, such fillers are sometimes used to confer flame retardancy and could of course increase k_s. An appropriate mixing rule is needed for calculation of k_s such as those in Taylor's [4] and Mottram and Taylor's [5] reviews whereupon its effect is shown in Fig. 6. Thus the overall effect of a mineral filler of higher conductivity than the matrix at loadings of ~ 10 vol % based on the polymer is slight. It may be thought that the addition of a filler would have a deleterious effect on the biaxial extensional viscosity and hence on foam manufacture, but recent work has shown that thermoplastic polymers with filler loadings in the region of 50-59 vol % can be subjected to manufacturing operations which involve extensional flows namely vacuum forming [83], blow moulding [84] and tubular film blowing [85].

The effect of polymer emissivity is explicitly described by Equations 23 and 39, and the dependence is shown in Fig. 8 for the foam of intermediate density DP8436. Clearly, surfaces with lower absorption reduce the radiative contribution. As before, some fillers may increase reflectivity as well as reducing transmission. Similarly, the incorporation of reflective layers into an insulator may be advantageous. This is a strategy adopted in the space-shuttle-thermal-protection system, wherein platelets of silicon carbide are incorporated into the silica-fibre mat [86].

Insufficient information was available to give a proper assessment of the polyimide foam, the transmission being uncertain. A value of $t = 0.75$ (in the

TABLE II Calculated radiation contributions to cellular materials

Material	Grade	Calculated radiative contributions									
		Equation number								$\bar{k}_r^c$	$\bar{k}_r/k$ (%)^d
		23	25	27^a	27^b	28	31	34	39		
Polyurethane	RM126	0.005	0.006	0.004	0.003	0.005	0.005	0.001	0.001	0.0047	26
Polyurethane	RM130	0.006	0.004	0.003	0.002	0.006	0.006	0.001	0.002	0.0045	23
Polyurethane	DP8436	0.003	0.002	0.002	0.001	0.003	0.003	0.001	0.001	0.0023	11
Polyurethane	PE406W	0.005	0.002	0.002	0.001	0.005	0.005	0.001	0.001	0.0033	12
Polyurethane	RM500	0.005	0.001	0.001	0.001	0.005	0.005	0.001	0.001	0.0030	9
Polyurethane	RM520	0.004	0.001	0.001	0.001	0.004	0.003	0.001	0.001	0.0023	6
Polyimide	Solimide^e	0.006	0.021	0.011	0.010	0.014	0.011	0.001	0.002	0.0012	29
Polyethylene	L70	0.47	–	–	–	0.19	0.21	0.11	0.13	–	–

^{a} $k = 6 \times 10^4$.
^{b} $k = 16 \times 10^4$.
^{c} Average of k_r, excluding Equations 34 and 39, as a percentage of the measured conductivity.
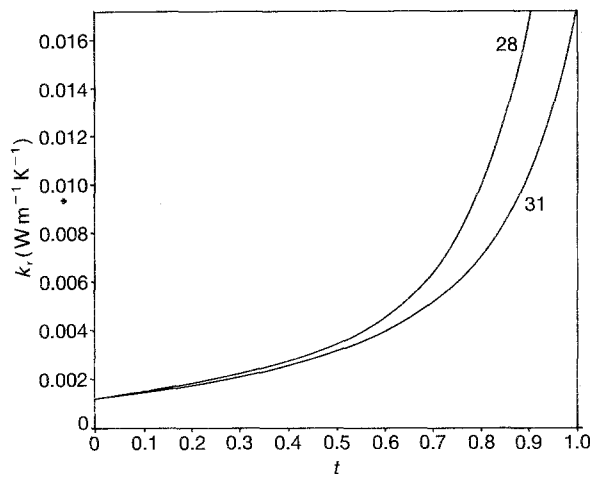^{d} Expressed as a percentage of measured conductivity.
^{e} $t = 0.75$.

Figure 7 The effect of the transmission on the radiative contribution to the apparent conductivity for the polyurethane foam DP8436. The curves are labelled with equation numbers from the text.
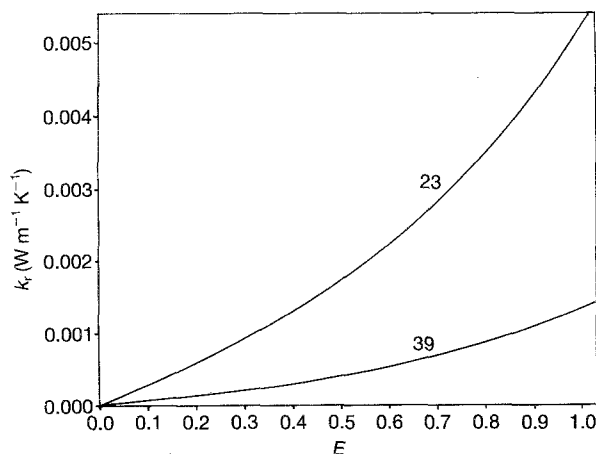

Figure 8 The effect of emissivity on the radiative contributions to apparent conductivity for polyurethane foam DP8436. Curves are labelled with equation numbers from the text.

upper range for polymers) was arbitrarily selected for the calculation in Equations 28 and 31, but this still fails to explain the high measured conductivity for such a low-density foam. The foam has a very wide spread of cell diameters, while the equations only

accept a single mean value. However, the sensitivity to the cell size is not great. Taking air as the cell gas, the conductivity contributions from 14 equations give $k_c = 0.028 \pm 0.0008$ W m^{-1} K^{-1}. Only Equation 25, which employs a predicted foam extinction coefficient based on data for polyurethane, would then give a sufficiently high radiation contribution ($k_r = 0.021$ W m^{-1} K^{-1}) to give a total apparent conductivity of 0.05 W m^{-1} K^{-1} to compare with the quoted measurement of 0.042 W m^{-1} K^{-1}. If this assessment be valid the foam would clearly benefit from an opacifier or some other means of reducing the radiative contribution.

The polyethylene blister packaging, which is of the coarse variety ($L_g = 25$ mm), presents an extreme situation. The average conduction contribution is also 0.028 ± 0.008 W m^{-1} K^{-1} for air as the cell gas. This is because of the very low solids content. The radiation calculations yield high results because the condition $L \gg L_g$ is not met. The large cell size is also consistent with a significant convective-heat-transport contribution to the apparent conductivity, as predicted for cells greater than 4 mm in diameter.

7. Conclusion

Diverse equations for the conduction contributions to the apparent conductivity for polyurethane foams have been assessed, and in the voidage region 0.8 to 1.0 seven of these show good agreement with the measured apparent conductivities of commercial polyurethane foams. Of these, an expression due to Batty et al. which models the distribution of a solid in a foam shows good agreement with experiment. The radiative contributions calculated from five out of seven of the suggested expressions also show good internal agreement and suggest that radiation contributes 6–26% of the apparent conductivity depending inversely on solids content. The effects of gas and solid conductivities, emissivity and transmittance on the apparent conductivity have been explored. The expressions for conductive and radiative contributions offer guidance on the material and structural interventions which

promise reduced apparent conductivity in the context of legislative restrictions on blowing agents.

Acknowledgements

References

1. House of Commons Energy Committee, Sixth Report, Energy Policy Implications of the Greenhouse Effect (Her Majesty's Stationery Office, London 1989) Vol. 1, para. 102.
2. R. C. PROGELHOF, J. L. THRONE and R. R. RUETSCH, *Polym. Engng. Sci.* **16** (1976) 615.
3. D. K. HALE, *J. Mater. Sci.* **11** (1976) 2105.
4. R. TAYLOR, in "International encyclopedia of composites", edited by S. M. Lee Vol. 5, (VCH, New York, 1991) pp. 530–548.
5. J. T. MOTTRAM and R. TAYLOR, *ibid.* Vol. 5, (VCH, New York, 1991) pp. 476–496.
6. R. A. CRANE, R. I. VACHON and M. S. KHADER, Proceedings of the Seventh Symposium on Thermophysical Properties, Galthersberg, MD, USA (American Society for Mechanical Engineers, NY, USA, 1977) pp. 109–123.
7. J. A. VALENZUELA and L. R. GLICKSMAN, in Thermal Insulation, Materials and Systems for Energy Conservation in the 80's, ASTM STP 789, edited by F. A. Govan, D. M. Greason, J. D. McAllister (American Society for Testing and Materials, Philadelphia, USA) pp. 688–702.
8. J. C. MAXWELL, "A treatise on electricity and magnetism", Vol. 1 (Clarendon Press, Oxford 1892) p. 440.
9. W. WOODSIDE and J. H. MESSMER, *J. Appl. Phys.* **32** (1961) 1688.
10. A. V. LIUKOV, A. G. SHASHKOR, L. L. VASILIEV and YU. E. FRAISMAN *Int. J. Heat Mass Transfer* **11** (1968) 117.
11. R. L. HAMILTON and O. K. CROSSER, *Ind. Engng. Chem. Fundam.* **1** (1962) 187.
12. D. TABOR, "Gases, liquids and solids", 2nd Edn (Cambridge University Press, Cambridge, 1979) p. 57.
13. M. E. STEPHENSON and M. MARK, *Amer. Soc. Heat., Refrig. Air Conditioning Engineers J.,* 3 February (1961) 75.
14. G. T-N. TSAO, *Ind. Engng. Chem.* **53** (1961) 395.
15. A. SUGAWARU and Y. YOSHIZAWA, *J. Appl. Phys.* **33** (1962) 3135.
16. A. W. PRATT, in "Thermal conductivity, "edited by R. P. Tye, Vol. 1 (Academic Press, London 1969) p. 319.
17. C. H. LEES, *Phil. Mag.* **49** (1900) 221.
18. Z. HASHIN and S. SHTRIKMAN, *J. Appl. Phys.* **33** (1962) 3125.
19. D. J. DOHERTY, R. HURD and G. R. LESTER, *Chem. Ind.* July (1962) 1340.
20. S. BAXTER and T. T. JONES, *Plastics Polym.* **40** (1972) 69.
21. F. K. BROCKHAGEN and W. SCHMIDT, in "Polyurethane Foams", edited by T. T. Healy (Iliffe, London, 1964) pp. 93–144.
22. E. KERNER, *Proc. Phys. Soc. B* **369** (1956) 802.
23. A. D. BRAILSFORD and K. G. MAJOR, *Brit. J. Appl. Phys.* **15** (1964) 313.
24. T. ZHANG, J. R. G. EVANS and K. K. DUTTA, *J. Euro. Ceram. Soc.* **5** (1989) 303.
25. R. HAMILTON and O. CROSSER, *Ind. Engng. Chem. Fundam.* **1** (1962) 187.
26. M. H. KUOK, H. K. SY and K. L. TAN, *Reg. J. Energy, Heat Mass Transfer* **7** (1985) 17.
27. S. OKA and K. YAMONE, *Jpn. J. Appl. Phys.* **6** (1967) 469.
28. R. M. BARRER, in "Diffusion in polymers" Edited by J. Crank and G. S. Park, (Academic Press, London 1968) pp. 165–216.
29. Von D. A. G. BRUGGEMAN, *Ann. Phys.* **5** (1935) 636.
30. R. C. PROGELHOF and J. L. THRONE, *J. Cell. Plast.* **11** (1975) 152.
31. A. EUCKEN, *Forsch. Gebiete Ingenieuru B3 Forschurgshaft No.* **353** (1932) 16.
32. H. W. RUSSELL, *J. Amer. Ceram Soc.* **18** (1939) 1.
33. B. BUDIANSKY, *J. Compos. Mater.* **4** (1970) 286.
34. T. B. JEFFERSON, O. W. WITZELL and W. L. SIBBITT, *Ind. Engng. Chem.* **50** (1958) 1589
35. L. TOPPER, *Ind. Engng. Chem.* **47** (1955) 1377.
36. S. C. CHENG and R. I. VACHON, *Int. J. Heat Mass Transfer* **13** (1970) 537.
37. D. BEDEAUX and R. KAPRAL, *J. Chem. Phys.* **79** (1983) 1783.
38. L. E. NIELSEN, *J. Appl. Polym. Sci.* **17** (1973) 3819.
39. *Idem., Ind. Engng. Chem. Fundam.* **13** (1974) 17.
40. *Idem., Appl. Polym. Symp.* **12** (1966) 249.
41. J. M. PETERSON and J. J. HERMANS, *J. Compos. Mater.* **3** (1969) 338.
42. M. M. LEVY, *J. Cell. Plastics* **2** (1966) 37.
43. D. BHATTACHARJEE, J. A. KING and K. N. WHITEHEAD, *ibid.* **27** (1991) 240.
44. R. J. HARDING, *ibid.* **1** (1965) 224.
45. *Idem., ibid.* **1** (1965) 385.
46. F. J. NORTON, *ibid.* **3** (1967) 23.
47. C. J. HILADO and W. R. PROOPS, *ibid.* **5** (1969) 299.
48. G. W. BALL, R. HURD and M. G. WALKER, *ibid.* **6** (1970) 66.
49. R. R. DIXON, L. E. EDELMAN and D. K. McLAIN, *ibid.* **6**, (1970) 44.
50. M. BOMBERG, *ibid.* **26** (1990) 275.
51. T. T. JONES, *Plastics Polym.* **40** February (1972) 33.
52. R. BOETES and C. J. HOOGENDOORN, *Proc. Int. Cent., Heat Mass Trans.* **24** (1987) 14.
53. L. GLICKMAN, M. SCHUETZ and M. SINOFSKY, *Int. J. Heat Mass. Trans.* **30** (1987) 187.
54. M. A. SCHUETZ and L. R. GLICKSMAN, *J. Cell. Plast.* **20** (1984) 114.
55. L. R. GLICKSMAN, *Cellular Polym.* **10** (1991) 276.
56. A CUNNINGHAM, *Proc. Int. Cent. Heat Mass Trans.* **24** (1987) 32.
57. R. J. J. WILLIAMS, C. M. ALDAO, *Polym. Engng. Sci.* **23**, (1983) 293.
58. M. GARBUNY, "Optical Physics", (Academic Press, NY, 1965) p. 257.
59. A. L. LOEB, *J. Amer. Ceram. Soc.* **37** (1954) 96.
60. J. FRANCL and W. D. KINGERY, *ibid.* **37** (1954) 99.
61. W. J. BATTY, S. D. PROBERT and P. W. O'CALLAGHAN, *Appl. Energy* **18** (1984) 117.
62. R. J. HARDING, *J. Cell. Plast.* **2** (1966) 206.
63. R. CAPS, A. TRUNGER, D. BUTTNER and J. FRICKE, *Int. J. Heat and Mass Transf.* **27** (1984) 1865.
64. J. FRICKE, R. CAPS, D. BUTTNER, U. HEINEMANN and E. HUMMER, *J. Non-Cryst. Sol.* **95–96** (1987) 1167.
65. R. CAPS and J. FRICKE, *Solar Energy* **36** (1986) 361.
66. T. W. TONG and C. L. TIEN, *Trans. ASME Ser. C. J. Heat Transfer* **105** (1983) 70.
67. T. W. TONG, Q. S. YANG and C. L. TIEN, *ibid.* **105** (1983) 76.
68. R. W. SKOCHDOPOLE, *Chem. Engng. Prog.* **57**(10) (1961) 55.
69. H. JEFFREYS, *Proc. Roy. Soc. A.* **118** (1928) 195.
70. T. T. HEALY, "Polyurethane foams (Iliffe, London, 1964) p. 121.
71. Anon, The properties of Dupont Vespel Parts, Technical Data Sheet (Dupont, Wilmington, DE, Undated).
72. J. FRICKE, *J. Non-Cryst. Solids* **100** (1988) 169.
73. R. C. WEAST (editor) Handbook of Chemistry and Physics", 55th Edn (CRC Press, Cleveland, Ohio 1974) p. E2.
74. C. R. WILKE, *J. Chem. Phys.* **18** (1950) 517.
75. *Loc. cit.* [12], pp. 69–70.
76. J. FRICKE in Proceedings of the First International Symposium on Aerogels at Wurzberg 1985, edited by J. Fricke (Springer Verlag, Heidelberg, 1986) pp. 94–103.
77. D. BUTTNER, R. CAPS, U. HEINEMANN, E. HUMMER, A. KADUR and J. FRICKE, *Solar Energy* **40** (1988) 13.

78. D. BUTTNER, R. CAPS and J. FRICKE, *High Temp. High Pressures* **17** (1985) 375.
79. J. BRANDRUP and E. H. IMMERGUT, "Polymer Handbook", 2nd Edn (Wiley, New York, 1974) p. VIII-9.
80. C. A. DOSTAL (editor) "Engineered Materials Handbook", Vol. 2 (American Society for Metals, Metals Park, Ohio, 1988) p. 260.
81. *Loc. cit.* [80], p. 133.
82. BS874 Part 2, Tests for Thermal Conductivity and Related Properties, Section 2.1, Guarded hot plate method, (British Standards Institute, London, 1986).

83. K. M. HAUNTON, J. K. WRIGHT and J. R. G. EVANS, *Brit. Ceram. Trans. J.* **89** (1990) 53.
84. P. HAMMOND and J. R. G. EVANS, *J. Mater. Sci. Lett.* **10** (1991) 294.
85. J. GREENER and J. R. G. EVANS, *J. Mater. Sci.* in press.
86. W. SCHRAMM, *Bull. Amer. Ceram. Soc.* **60** (1987) 1194.