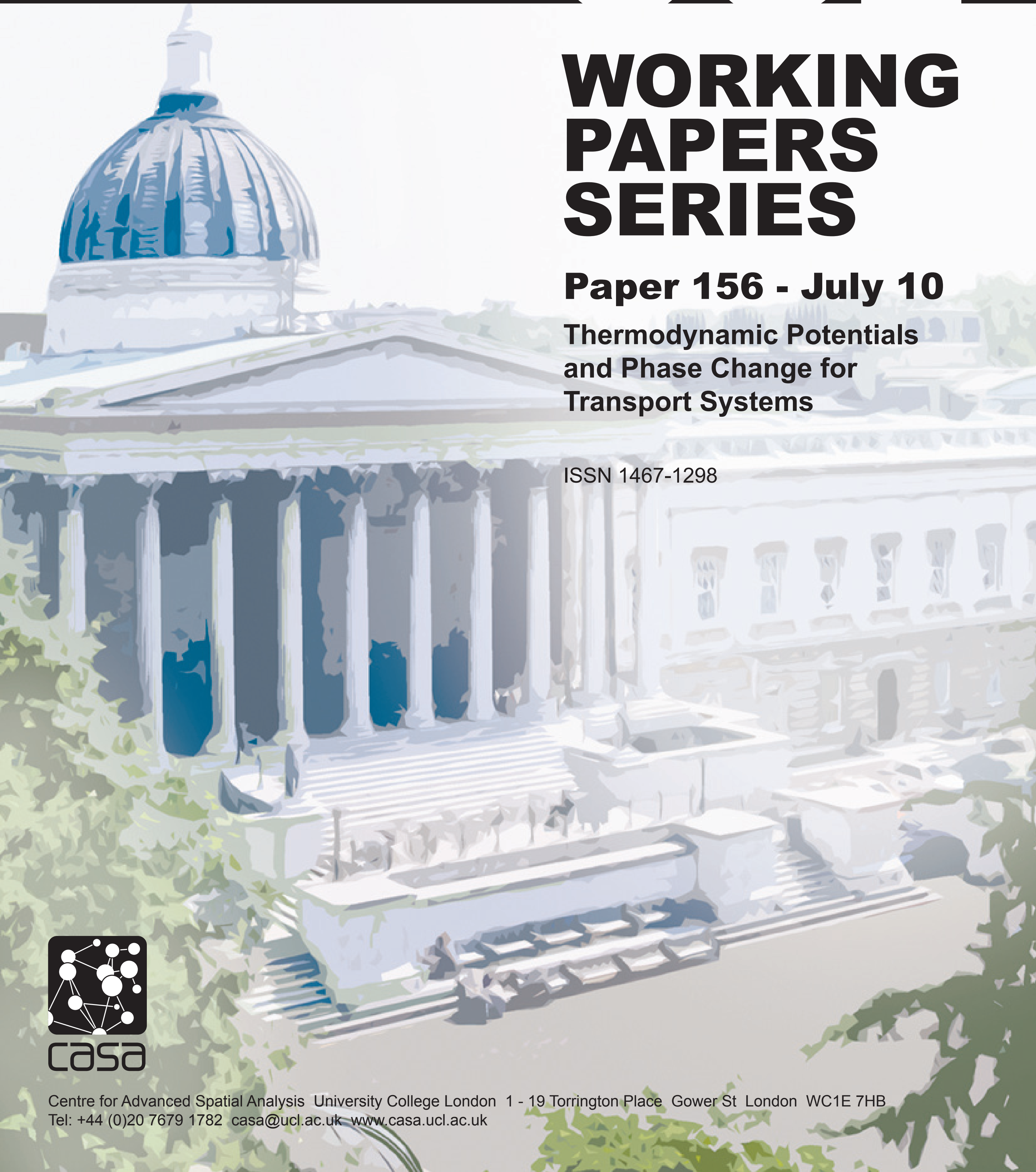
UCL CENTRE FOR ADVANCED SPATIAL ANALYSIS

UCL

WORKING PAPERS SERIES



Paper 156 - July 10

Thermodynamic Potentials and Phase Change for Transport Systems

ISSN 1467-1298

casa

Centre for Advanced Spatial Analysis University College London 1 - 19 Torrington Place Gower St London WC1E 7HB
Tel: +44 (0)20 7679 1782 casa@ucl.ac.uk www.casa.ucl.ac.uk

Thermodynamic Potentials and Phase Change for Transport Systems[1]

Robin Morphet[2]
rmjm Consulting

1. Introduction

"Thermodynamics of the City" (Wilson 2008) poses the question, in relation to the doubly constrained trip distribution model –What is Z?- where Z is the partition function. To answer this question the entropy maximising procedure of Jaynes(1957) is employed, the partition function derived and expressions given for Helmholtz free energy, for more general free energies and for specific heat. Phase changes are identified using these measures. The implications of these results are discussed and the possibility of a spatially based exergy analysis is suggested .

2. The Doubly Constrained Model

In the doubly constrained model the area of study is divided into zones and trips T_{ij} , are modelled from origin zone i , to destination zone j. The number of origins O_i , in each zone is given as are the number of destinations, D_j . The model is formulated as

$$T_{ij} = A_i O_i B_j D_j f\left(c_{ij}\right) \tag{1}$$

In this formulation $f(c_{ij})$ is the deterrence function which reflects the impact of the cost of travel, c_{ij} , between zones i and j . In what follows we take

$$f\left(c_{ij}\right) = e^{-\beta c_{ij}} \tag{2}$$

the conventional formulation for the deterrence function and the conventional form in the statistical mechanical development of thermodynamics. However, the analysis may also be extended to other forms

The constraints to which this model must conform are

[2] Robin Morphet is an Honorary Research fellow in CASA, contact r.morphet@ucl.ac.uk

$$\sum_j T_{ij} = O_i \tag{3}$$

$$\sum_i T_{ij} = D_j \tag{4}$$

$$\sum_i \sum_j T_{ij} c_{ij} = C \tag{5}$$

The final constraint is one of total generalised cost and in this formulation, generalised cost is an analogue of energy in thermodynamics.

3. The Maximum Entropy Formulation

The above model has been formally derived (Wilson, 1970) and its assumptions explained. The derivation below is slightly different and follows the derivation of Jaynes (Jaynes, 1982). In this the additional and seemingly redundant constraint of equation (6) is added thus:

$$\sum_i \sum_j T_{ij} = N \tag{6}$$

where N is the total number of trips. In the standard model this summation is implicit in the data used for O_i and D_j and in the iterative estimation of the model. However, as Jaynes makes clear, under entropy maximisation, the information contained in the algebraic expression of the model is only that contained in the constraints, no more and no less (Jaynes, 1957). It therefore makes sense to incorporate (6) as this is information consistent with our observation of the system and as we shall see it allows us to derive the partition function. In order to maximise entropy with respect to these constraints we use the Lagrange multiplier equation.

$$L = -\sum_i^n \sum_j^m p_{ij} ln p_{ij} + \lambda_0 \sum_i \sum_j p_{ij} - 1 + \sum_i^n \lambda_i \left(p_{i*} - \sum_j^m p_{ij} \right) + \sum_j^m \lambda_j \left(p_{*j} - \sum_i^n p_{ij} \right) + \beta \left(C - \sum_i^n \sum_j^m p_{ij} c_{ij} \right) \tag{7}$$

in which $p_{ij} = \frac{T_{ij}}{N}$, $p_{i*} = \frac{O_i}{N}$, and $p_{*j} = \frac{D_j}{N}$. In this mode p_{ij} is the probability of a single trip going from zone i to zone j. The cost constraint is now a constraint on average cost from which we derive the maximum entropy distribution

$$p_{ij} = e^{-\lambda_0 - \lambda_i - \lambda_j - \beta c_{ij}} \tag{8}$$

We may then set up the partition function Z as follows

$$Z_c = \sum_i \sum_j e^{-\lambda_i - \lambda_j - \beta c_{ij}} \tag{9}$$

where the subscript c refers to the doubly constrained nature of the model and

$$\lambda_0 = \ln Z_c \tag{10}$$

giving the model

$$p_{ij} = \frac{e^{-\lambda_i - \lambda_j - \beta c_{ij}}}{Z_c} \tag{11}$$

The partition function behaves in the same way as the thermodynamic partition function in that the constraints are retrieved by differentiation of $\ln Z$. Thus

$$\frac{-\partial \ln Z_c}{\partial \beta} = \sum_i \sum_j p_{ij} c_{ij} \tag{12}$$

$$-\frac{\partial \ln Z_c}{\partial \lambda_i} = \frac{\sum_i \sum_j e^{-\lambda_i - \lambda_j - \beta c_{ij}}}{Z_c} = \sum_i \sum_j p_{ij} = 1 = \sum_i \sum_j e^{-\lambda_0 - \lambda_i - \lambda_j - \beta c_{ij}} = \sum_i e^{-\lambda_i} \sum_j e^{-\lambda_0 - \lambda_j - \beta c_{ij}} \tag{13}$$

and hence

$$e^{-\lambda_i} = (\sum_j e^{-\lambda_0 - \lambda_j - \beta c_{ij}})^{-1} \tag{14}$$

Equation (13) corresponds to the standard expressions (Wilson 1970) for the balancing factors

$$A_i = [\sum_j B_j D_j e^{-\beta c_{ij}}]^{-1} \tag{15}$$

and similarly

$$B_j = [\sum_j A_i O_i e^{-\beta c_{ij}}]^{-1} \tag{16}$$

It is convenient to write the partition function as

$$Z_c = \sum_i \sum_j r_i s_j e^{-\beta c_{ij}} \tag{17}$$

which reflects the form of the standard trip distribution model where

$$r_i = A_i O_i \tag{18}$$

and

$$s_j = B_j D_j \tag{19}$$

Using a single trip/particle model as a first step, has a number of advantages. Firstly, the absence of other particles obviates the need to consider any interactions. Secondly, with only one particle, considerations of distinguishability and indistinguishability do not arise.

4. Defining Helmholtz Free Energy

Having defined the partition function the model follows thus

$$p_{ij} = \frac{r_i s_j e^{-\beta c_{ij}}}{Z_c} \tag{20}$$

with Z_c playing the role of a normalising constant. From equation (20) we may write

$$\ln p_{ij} = (\ln r_i s_j - \beta c_{ij} - \ln Z_c) \tag{21}$$

hence the entropy, S is given by

$$
\begin{aligned}
S &= -<\ln p_{ij}> = \sum_i \sum_j p_{ij}(-\ln r_i s_j + \beta c_{ij} + \ln Z_c) \\
&= \sum_i \sum_j p_{ij}(-\ln r_i s_j + \beta c_{ij}) + \ln Z_c \\
&= <-\ln r_i s_j + \beta c_{ij}> + \ln Z_c \\
&= -<\ln r_i s_j> + \beta U + \ln Z_c
\end{aligned} \tag{22}
$$

where

$$<\ln rs> = \sum_i \sum_j p_{ij} \ln\left(r_i s_j\right) \tag{23}$$

and U is the total internal energy. Hence, starting from equation (20) we have derived the expression

$$U - \frac{1}{\beta} S = \frac{1}{\beta}(<\ln r_i s_j> - \ln Z_c) \tag{24}$$

If $\frac{1}{\beta}$ is taken as temperature then the left hand side of equation (24) may be written as $U - TS = F$ (25)

where U is the total energy, T is the temperature and F is the free energy given by

$$F = T(<\ln r_i s_j> - \ln Z_c) \tag{26}$$

In the unconstrained case the λ_i and λ_j of equation (9) go to zero so the $\ln r_i s_j$ term also disappears giving

$$F = -T \ln Z_u \tag{27}$$

where $Z_u = \sum_i \sum_j e^{-\beta c_{ij}}$ (28)

the partition function for the unconstrained model, which may be compared with the standard thermodynamic definition (Cowan 2005) of

$$F = -kT \ln Z \tag{29}$$

In this equation F is the Helmholtz free energy and k is Boltzmann's constant which (Jaynes 1957) 'may be regarded as a correction factor necessitated by our custom of measuring temperature in arbitrary units'. We may thus define k as unity which ensures that entropy is dimensionless and that temperature or $\frac{1}{\beta}$ has the same dimensions as c_{ij}. This is consistent with the definition of temperature as a measure of the average kinetic energy of the particles in an ideal gas. An alternative name for Helmholtz free energy is *Arbeit*, the German for work, as the free energy is the maximum energy available for work. Helmholtz free energy is often denoted by *A*, a convention which we will follow when it aids clarity. We may thus write for the unconstrained model

$$A = -\frac{1}{\beta}\ln Z_u \tag{30}$$

We may unpack equation (24) a little further by writing it as

$$U - \frac{1}{\beta}S = \frac{1}{\beta}\left(\sum_i\sum_j -\lambda_i.p_{ij} + \sum_i\sum_j -\lambda_j.p_{ij} - \ln Z_c\right) \tag{31}$$

which may be interpreted as a left hand side identifying kinetic energy terms and a right hand side identifying potential or available energy terms. The right hand side shows an origin related term and a destination related term plus the free energy associated with the interchange. If we now take the origin term over to the left hand side and writing

$$U_{\lambda_i} = \sum_i\sum_j p_{ij}\left(c_{ij} + \frac{\lambda_i}{\beta}\right) \tag{32}$$

we get

$$U_{\lambda_i} - \frac{1}{\beta}S = \frac{1}{\beta}\left(\sum_i\sum_j -\lambda_j.p_{ij} - \ln Z_c\right) \tag{33}$$

so the energy involved in adjusting the origins of the unconstrained model to those of the origin constrained model , is now contained within the internal or kinetic energy term. Continuing the process to incorporate the destination constraints we may write

$$U_{\lambda_i\lambda_j} - \frac{1}{\beta}S = -\frac{1}{\beta}\ln Z_c \tag{34}$$

This gives us the constrained model in an unconstrained formulation with cost $c_{ij}^{/}$ given by

$$c_{ij}^{/} = c_{ij} + \frac{\lambda_i}{\beta} + \frac{\lambda_j}{\beta} \tag{35}$$

that is by an interchange cost, an origin cost and a destination cost. The internal energy now includes the potential energy (as it should (Keenan, 1956) if the energy is in the form of heat or work, i.e. an energy which has its associated entropy change) and may thus be likened to enthalpy (see equation (55)). It should be noted that the origin and destination costs should not be interpreted simply as terminal costs but rather as the cost in transport terms of achieving the given pattern of origins and destinations. They might be regarded as the transport costs of location or the transport element of the rent and as such could include any terminal costs such as parking. If such costs are included in the cost matrix they will add an element of biproportionality to the matrix and will then be absorbed by the balancing factors in the doubly constrained model. This line of argument has been advanced before (Dieter, 1962) but it has been argued (e.g. Kirby, 1970) that the balancing factors cannot be costs associated with the origins or destinations as, when incorporated into the cost matrix, new balancing factors will be produced under the doubly constrained model. However, this is not correct as, if the balancing factors are absorbed into the cost matrix as in equation (35) , the correct model formulation is the unconstrained model. If r_i and s_j are completely absorbed into the cost matrix then the unconstrained model will give the same results as the doubly constrained model using the original cost matrix. It should also be noted that in equations (31) to (34) the entropy, S, remains the same with its probability function incorporating both constraints as in equation (11). The unconstrained model with the costs including both constraint costs, as set out above, will reproduce the results of the constrained iteration and this is demonstrated in Appendix 1.

5. Ensembles in urban transport models

Ensembles in thermodynamics are used to classify the nature of the system under consideration and also as a way of introducing frequency arguments. It could be argued that both of these approaches are unnecessary. The underlying concepts are Bayesian (Jaynes, 1957) needing no frequentist underpinning and the characteristics of the system can be described without reference to an ensemble. Indeed we might argue that all our knowledge of the system is contained in the Lagrange multiplier equation or in the partition function. However, given the extensive use made of ensembles in thermodynamic analysis , it is useful to locate entropy maximising transport models in this kind of framework . This allows us to develop our analysis using statistical mechanics as a suggested itinerary rather than a route map.

If we consider an ideal gas at equilibrium then any one portion of it, defined by an imaginary envelope, will be indistinguishable from any other part of it. Within the envelope average internal energy and temperature will be the same as outside. If the envelope were now to become real, rigid and a thermal barrier, the enclosed volume would have the same temperature and volume as before but would now also have a pressure generated by the internal energy of the enclosed molecules. The system would be isolated from its surroundings but indistinguishable from them. The pressure would be exactly balanced by the pressure of the surrounding gas and the free energy would be zero. A number of such isolated systems together corresponds to the microcanonical ensemble.

However, in the analysis of transport models that follows it is the temperature β that is fixed and this corresponds to the canonical ensemble which is defined by its location of the system of interest, in a constant temperature heat bath (Sethna, 2008). That β is fixed in transport modelling is evident from its use as an invariant in the projection of trips after cost and origin and destination changes. In the first case, the microcanonical case, the internal energy determines the value of β. In the second case, the canonical case, temperature is set by the heat bath of the surrounding gas and each system in the ensemble has a heat permeable envelope (MacDonald, 2006). Generally, the use of Helmholtz free energy implies a canonical ensemble (MacDonald, 2006) where temperature change in the heat bath (comprised of similar systems) allows heat energy transfer across the system envelope. Indeed, the canonical representation is sometimes described as the Helmholtz representation (Callen, 1985). In equation (7) the final constraint shows that the *average* energy is constrained and hence the approach is canonical (Sornette, 2000).

Equation (30) acts as the bridging equation between micro and macro states. In the case of the constrained transport model, the constraints are created adding energy to the internal energy of the system with its temperature maintained at a constant by the heat bath. The heat bath corresponds to the time and money resources available in the economy in which the transport system is embedded. Similarly, any recourse to Gibbs free energy implies a grand canonical ensemble where not only is a similar transfer of energy permitted but particles can be interchanged, the particles themselves possessing energy. This latter kind of ensemble analysis may be useful in examining modal split in an entropy maximising context.

The external imposition of work on the system creates potential energy in the form of the constraints which is added to the internal energy thus increasing the system's potential for work. In effect the system has work done on it and this makes it distinguishable from its surroundings. A similar argument is advanced by Tribus (Tribus and McIrvine, 1971). The heat bath may be seen as a lake of energy , the 'wine bottle in a swimming pool' analogy. Alternatively, it may be seen as a collection of similar systems each exchanging energy with themselves and the system of interest, to maintain the constant average temperature. The first view seems sufficient for our purposes as it effectively situates the system of interest, the city, within the heat bath of its economy. The second view would correspond more nearly to the idea of 'cities as systems within systems of cities' (Berry,1964).

Another, possibly more familiar, way to consider the ensembles is to see the microcanonical ensemble as a closed system with all its parameters determined internally. The canonical ensemble may then be seen as an open system, open to heat transfers to and from the heat bath. The grand canonical ensemble might then be seen as an open system within an environment of similar open systems with particle, heat and other energy transfers being possible between the system of interest and its surrounding systems.

6. Multiple Trips

The question arises of how expressions in equations (24) and (26) might change when we consider more than one trip, i.e. when we move from the single particle analysis to the multiparticle case. Following Cowan (Cowan 2005) it might be argued that the multiparticle partition function Z_m is given by

$$Z_m = Z_s^N \tag{36}$$

where N is the number of trips/particles. However, this is only the case when the trips/particles are distinguishable. In the indistinguishable case we get

$$Z_m = \frac{1}{N!} Z_s^N \tag{37}$$

following Cowan (Cowan 2005).

The following derivation shows how the formulation of equation (26) arises naturally in moving from entropy expressed as $-\sum_i \sum_j p_{ij} \ln p_{ij}$ to entropy expressed as $-\sum_i \sum_j T_{ij} \ln T_{ij}$ i.e. moving from the single particle to the multiparticle canonical representation. However the use of $-\sum_i \sum_j T_{ij} \ln T_{ij}$ for entropy, although appropriate for variational analysis, is not complete. Taking

$$w = \frac{N!}{\prod_{ij} T_{ij}!} \tag{38}$$

as the number of potential states of the system (Wilson 1970) we accept the definition of entropy S, as

$$S = \ln w = N \ln N - \sum_i \sum_j T_{ij} \ln T_{ij} \tag{39}$$

The single particle relationship expressed in equation (24) may be written, in the unconstrained case, as

$$U - \frac{1}{\beta} S = -\frac{1}{\beta} \ln Z_u \qquad (40)$$

which may be expressed as

$$\sum_i \sum_j p_{ij} c_{ij} - \frac{1}{\beta}(-\sum_i \sum_j p_{ij} \ln p_{ij}) = -\frac{1}{\beta} \ln Z_u \qquad (41)$$

multiplying all through by N we get

$$\sum_i \sum_j T_{ij} c_{ij} - \frac{1}{\beta}(-\sum_i \sum_j T_{ij} \ln p_{ij}) = -\frac{N}{\beta} \ln Z_u \qquad (42)$$

adding $\frac{1}{\beta} N \ln N$ (which equals $\frac{1}{\beta} \sum_i \sum_j T_{ij} \ln N$) to both sides, gives

$$\sum_i \sum_j T_{ij} c_{ij} + \frac{1}{\beta}(\sum_i \sum_j T_{ij} \ln T_{ij}) = -\frac{N}{\beta} \ln Z + \frac{1}{\beta} N \ln N \qquad (43)$$

which may be written

$$\sum_i \sum_j T_{ij} c_{ij} + \frac{1}{\beta}(\sum_i \sum_j T_{ij} \ln T_{ij} - N \ln N) = -\frac{N}{\beta} \ln Z_u \qquad (44)$$

The right hand side corresponds (Cowan 2005) to the expression for the free energy for distinguishable particles and has been derived algebraically from the single particle case . The left hand side includes the entropy $S = N \ln N - \sum_i \sum_j T_{ij} \ln T_{ij}$, the form similar to that used in spatial interaction modelling. In the doubly constrained case we have

$$\sum_i \sum_j p_{ij} c_{ij} - \frac{1}{\beta}(-\sum_i \sum_j p_{ij} \ln p_{ij}) = \frac{1}{\beta}(< \ln rs > - \ln Z_c) \qquad (45)$$

multiplying by N gives

$$\sum_i\sum_j T_{ij}c_{ij} - \frac{1}{\beta}(-\sum_i\sum_j T_{ij}\ln p_{ij}) = \frac{N}{\beta}(<\ln rs> - \ln Z_c) \qquad (46)$$

adding $\frac{1}{\beta}N\ln N$ gives

$$\sum_i\sum_j T_{ij}c_{ij} + \frac{1}{\beta}(\sum_i\sum_j T_{ij}\ln T_{ij}) = \frac{N}{\beta}(<\ln rs> - \ln Z + \ln N) \qquad (47)$$

and hence as in equation (44)

$$\sum_i\sum_j T_{ij}c_{ij} + \frac{1}{\beta}(\sum_i\sum_j T_{ij}\ln T_{ij} - N\ln N) = \frac{N}{\beta}(<\ln rs> - \ln Z) \qquad (48)$$

The change of entropy expression from $-\sum_i\sum_j p_{ij}\ln p_{ij}$ to $N\ln N - \sum_i\sum_j T_{ij}\ln T_{ij}$ has, as might be expected, scaled up the free energy by a factor of N since free energy is an extensive rather than intensive variable. However, in variational analyses such as the differentiation involved in maximising entropy or the evaluation of changes in entropy, the terms in *lnN* have no effect as *N* is constant. For the most part the analysis in this paper concentrates on the single particle case as this simplifies the algebra and emphasises use of average cost as the cost constraint as implied by the use of the canonical ensemble.

7. Other Free Energies and Enthalpy

In equation (27) the free energy is that of a single particle monatomic gas; all the energy, *U*, is kinetic energy. In considering system dynamics we need to take into account potential energy. To approach this question we consider the standard thermodynamic expression for the grand canonical potential Ψ (Callen, 1985).

$$\Psi = U - TS - \sum_i \mu_i N_i \qquad (49)$$

where $\mu_i N_i$ refers to the chemical energy of N_i particles of type *i*

Equation (24) may be rewritten as

$$U - \frac{1}{\beta}S - \frac{1}{\beta}\langle \ln rs \rangle = -\frac{1}{\beta}Z_c \qquad (50)$$

in which form it resembles equation (49) for the grand canonical potential, with $\frac{1}{\beta}\langle \ln rs \rangle$ taking the place of the potential energy represented by the $\mu_i N_i$ terms thus

$$-\frac{1}{\beta}\langle \ln r_i s_j \rangle = \frac{1}{\beta}\sum_i \sum_j p_{ij}\left(\lambda_i + \lambda_j\right) \quad (51)$$

In equation (50) the positive value of U reflects an energy induced by work done on the system. As the origins migrate to the destinations work is done which by itself would lead to a temperature fall. However, the heat bath maintains the temperature thereby transferring energy to the system. In this approach we are adopting the physics rather than the engineering sign convention. Engineering, being concerned with work outputs, regards these as positive whereas in physics, such outputs are regarded as negative (Finn, 1986). The value of $\langle \ln r_i s_j \rangle$ will always be positive as λ_i and λ_j are positive and we may write

$$\sum_i \sum_j p_{ij} \ln r_i s_j = \sum_i \sum_j p_{ij} \ln\left(\frac{p_{ij} Z_c}{e^{-\beta c_{ij}}}\right) = I + \ln\left(\frac{Z_c}{Z_u}\right) \quad (52)$$

On the right hand side of equation (52)I is the expected information given by

$$I = \sum_i \sum_j p_{ij} \ln \frac{p_{ij}}{q_{ij}} \quad (53)$$

where

$$q_{ij} = \frac{e^{-\beta c_{ij}}}{\sum_i \sum_j e^{-\beta c_{ij}}} \quad (54)$$

the probability distribution of the unconstrained model. The expected information,*I*, is greater than 0 provided $p_{ij} \neq q_{ij}$ when it equals 0 (Theil, 1972). The final term, $\ln\left(\frac{Z_c}{Z_u}\right)$, may be positive or negative depending on whether or not $\left(\frac{Z_c}{Z_u}\right) > 1$. We may now write an expression for an enthalpy like function, *H*, that combines the kinetic and potential energies of the system thus

$$H = \sum_i \sum_j p_{ij} c_{ij} - \frac{1}{\beta}\langle \ln rs \rangle = \sum_i \sum_j p_{ij}\left(c_{ij} + \frac{\lambda_i + \lambda_j}{\beta}\right) \quad (55)$$

and we can then write, using equation(50)

$$H = F + TS \quad (56)$$

which shows that the energy input results in the production of entropy and free energy. Equation (55) again shows that we can formulate the doubly constrained model as an unconstrained model by using the cost function $\left(c_{ij} + \frac{\lambda_i + \lambda_j}{\beta}\right)$ instead of c_{ij}.

For Gibbs free energy, the chemical potential term in equation (49) is replaced by – PV giving $H = U + PV$.

In thermodynamics pressure, volume and chemical potential are state variables, unlike work which is path dependent. Taken together r_i and s_j are unique (Evans, A.W., 1970) and thus $\langle \ln r_i s_j \rangle$ is also unique, implying that for given values of β and c_{ij} the value is path independent. Thus $\langle \ln r_i s_j \rangle$ may be taken as being equivalent to a state variable .

Case	F
Single particle unconstrained	$-\frac{1}{\beta}\ln Z_u$
Single particle constrained	$\frac{1}{\beta}\langle \ln r_i s_j \rangle - \frac{1}{\beta}\ln Z_c$
Multiparticle unconstrained	$-\frac{N}{\beta}\ln Z_u$
Multiparticle constrained	$\frac{N}{\beta}\langle \ln r_i s_j \rangle - \frac{N}{\beta}\ln Z_c$
Note: $Z_c = \sum_i \sum_j r_i s_j e^{-\beta c_{ij}}$ with, in the unconstrained case, $r_i s_j = 1$ and $Z_u = \sum_i \sum_j e^{-\beta c_{ij}}$	

Table1: Free energy expressions

In Table 1 above F has been taken to include potential energy in line with the definition of availability (Keenan, 1942). However, we might equally write equation (50) as

$$U - \frac{1}{\beta}S - \frac{1}{\beta}\langle \ln r \rangle = -\frac{1}{\beta}Z_c + \frac{1}{\beta}\langle \ln s \rangle \quad (57)$$

according to where the system is in its progressive transmutation of origins into destinations. Equation (57) shows that the expenditure of the trip related kinetic energy and the origin related potential energy become the free energy, $-\frac{1}{\beta}Z_c$, and the destination related potential energy.

8. Defining a Generalised Free Energy

We have seen from equations (52) to (56) and the subsequent analysis that the free energy defined is not exactly equivalent to the Gibbs free energy potential, *G*, defined usually as

$$G = H - TS = U + PV - TS \tag{58}$$

This is because we do not have system wide equivalents of pressure and volume. The free energy associated with the biproportional model is closer to the grand canonical potential although any particle exchange is within the system between origins and between destinations(see section 10). It may therefore be useful to think of it as biproportional free energy. In this section we examine the nature of the free energy, *F*, implied by equation (52). Using equations (20), (51) and (52) we may write

$$-\frac{1}{\beta}\left\langle \frac{\ln r_i s_j}{Z_c} \right\rangle = -\frac{1}{\beta}\left\langle \ln r_i s_j \right\rangle + \frac{1}{\beta}\ln Z_c = -F \tag{59}$$

This gives an expression in units of energy as might be expected and all the potential energy applied to the system plus the free energy is equal to the energy available from the system. The equation might be deduced more directly from a comparison of equations (49) and (25). A plot of free energy against $\frac{1}{\beta}$ (diagram 1) is shown below. It shows that, at least for higher temperatures, *F* is a constant multiple of temperature. At very low temperatures, below 10 in this case, the linear relationship is not so clear cut. The low temperature behaviour is examined in more detail in section 10. What is happening is that as the temperature rises so β falls and so $e^{-\beta c_{ij}}$ rises. This emphasises the lower cost interchanges whose T_{ij} values increase at the expense of those of higher cost. The diagram shows results for an unconstrained model.
Equations (50) and (51) would appear to indicate that in most circumstances we cannot find separate expressions for P and V.[3]

[3] If equation (58) is expressed in matrix form it can be resolved. In particular if we consider the row formulation $-\frac{1}{\beta}\sum_j p_{ij} \ln p_{ij} e^{\beta c_{ij}} = P_i V_i$ then we may write p_{ij} as *P* and $\ln p_{ij} e^{\beta c_{ij}}$ as *C* then we may write $-\frac{1}{\beta} C.P = P_i V_i$. However this is not particularly useful for present purposes.

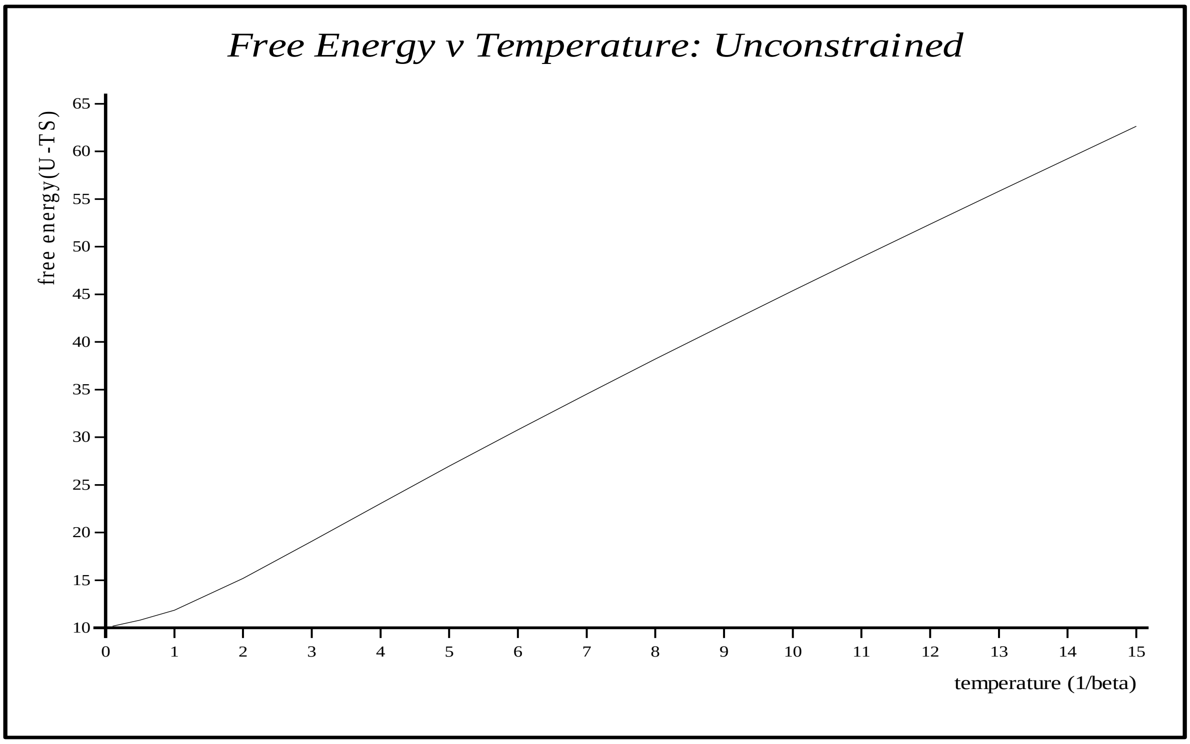


Diagram 1

However, if we let

$$q_{ij} = \frac{e^{-\beta c_{ij}}}{\sum_i \sum_j e^{-\beta c_{ij}}} = \frac{e^{-\beta c_{ij}}}{Z_u} \tag{60}$$

We may write, using equation (59)

$$-\frac{1}{\beta}\sum_i \sum_j p_{ij} \ln e^{\beta c_{ij}} = -\frac{1}{\beta}\sum_i \sum_j p_{ij} \ln \frac{p_{ij}}{q_{ij}} - p_{ij} \ln Z_u = -\frac{1}{\beta}\ln Z_u - \frac{1}{\beta}\sum_i \sum_j p_{ij} \ln \frac{p_{ij}}{q_{ij}} \tag{61}$$

Thus, up to a constant, the free energy *F,* is proportional to the expected information, *I*, where

$$I = \sum_i \sum_j p_{ij} \ln \frac{p_{ij}}{q_{ij}} \tag{62}$$

and again using equation (59), we may write

$$F = \frac{1}{\beta}\left(I - \ln Z_u\right) \tag{63}$$

A comparison with Table 1 shows that

$$I = \left\langle \ln r_i s_j \right\rangle \qquad (64)$$

which can be verified directly by using equation (20) to eliminate $r_i s_j$ from $\left\langle \ln r_i s_j \right\rangle$. In fact we could argue that as $-\frac{1}{\beta}\ln Z_u$ is the free energy of the unconstrained single particle, so F in equation (63), is the free energy induced through the work done in achieving the row and column constraints then being added to the free energy of the unconstrained case. Just as minimisation of free energy is equivalent to entropy maximisation so too is the minimisation of expected information (Morphet, 1975).

The identification of free energy with expected information (times temperature) allows the use of the decompositions set out by Theil (Theil, 1967, Theil 1972) which are shown, adapted for the transport model, in Appendix 4). We may therefore write equation (63) as

$$F = \frac{1}{\beta}\left(I_{O_i} - \ln Z_s + \sum_i p_{i*} I_i \right) = \frac{1}{\beta}\left(I_{D_j} - \ln Z_s + \sum_j p_{*j} I_j \right) \qquad (65)$$

Where p_{i*} and p_{*j} are defined as in equation (7) and

$$I_{O_i} = \sum_i p_{i*} \ln \frac{p_{i*}}{q_{i*}} \qquad (66)$$

and

$$I_i = \sum_j \frac{p_{ij}}{p_{i*}} \ln \frac{\frac{p_{ij}}{p_{i*}}}{\frac{q_{ij}}{q_{i*}}} \qquad (67)$$

This shows the free energy decomposed into a between origin (destination) component , a weighted within origin (destination) component and a system wide component of the unconstrained free energy. Theil (Theil, 1972) interprets the two elements of the decomposition of I as two steps in the modification of the original matrix. The first step transforms the matrix to a new origin distribution whilst the second transforms the revised matrix to give the new destinations.
We may write

$$I_{O_i} = \sum_i p_{i*} \ln \frac{p_{i*}}{q_{i*}} = \sum_i p_{i*} \frac{\sum_j \frac{r_i s_j e^{-\beta c_{ij}}}{Z_c}}{\sum_j \frac{e^{-\beta c_{ij}}}{Z_u}} = \sum_i p_{i*} \left(\frac{\sum_j r_i s_j e^{-\beta c_{ij}}}{\sum_j e^{-\beta c_{ij}}} - \ln Z_c + \ln Z_u \right) \tag{68}$$

if we now write

$$Z_{u_i} = \sum_j e^{-\beta c_{ij}} \tag{69}$$

and

$$Z_{c_i} = \sum_j r_i s_j e^{-\beta c_{ij}} \tag{70}$$

The two terms introduced are the row components of their respective partition functions. We may now write

$$I_{O_i} = \sum_i p_{i*} (\ln \frac{Z_{c_i}}{Z_c} - \ln \frac{Z_{u_i}}{Z_u}) \tag{71}$$

Turning our attention to equation (67) we may write

$$I_i = \sum_j \frac{p_{ij}}{p_{i*}} \ln \frac{\frac{r_i s_j e^{-\beta c_{ij}}}{\sum_j r_i s_j e^{-\beta c_{ij}}}}{\frac{e^{-\beta c_{ij}}}{\sum_j e^{-\beta c_{ij}}}} = \sum_j \frac{p_{ij}}{p_{i*}} \ln \frac{r_i s_j Z_{u_i}}{Z_{c_i}} \tag{72}$$

hence

$$I_i = \left\langle \ln r_i s_j \right\rangle_i + \ln Z_{u_i} - \ln Z_{c_i} \tag{73}$$

where

$$\left\langle \ln r_i s_j \right\rangle_i = \sum_i \frac{p_{ij}}{p_{i*}} \ln r_i s_j \tag{74}$$

Substituting from equations (71) and (73) into equation (65) we get

$$F = \frac{1}{\beta}\left(\left[\sum_i p_{i*}(\ln\frac{Z_{c_i}}{Z_c} - \ln\frac{Z_{u_i}}{Z_u})\right] - \ln Z_u + \left[\sum_i p_{i*}\left(\left\langle \ln r_i s_j \right\rangle_i + \ln Z_{u_i} - \ln Z_{c_i}\right)\right]\right)$$
$$= \frac{1}{\beta}\left(\sum_i p_{i*}\left(-\ln Z_c + \left\langle \ln r_i s_j \right\rangle_i\right)\right) = \frac{1}{\beta}\left(\left\langle \ln r_i s_j \right\rangle - \ln Z_c\right) \quad (75)$$

as before.

In equation (65) our energy analysis gives the first term (times temperature) as the work in free energy, required to construct the new origin distribution whilst the second term gives the work done to construct the new destination distribution using the free energy of the origin distribution. The work is done to the system and is added to the existing free energy as defined in equation (27). The source of the energy is the heat bath defined by the constant temperature parameter, β. The identification of the type of free energy as being Gibbs, Helmholtz, Landau, (Cowan, 2005), Keenan availability, (Keenan, 1956) or essergy (Evans, 1980), is unnecessary as the expected information formulation is general and incorporates all such free energies with the particular type being determined by the constraints in the Lagrange multiplier equation (Tribus and McIrvine, 1971[4]: Evans and Tribus,1965: Evans, 1980)) where, rather than maximising entropy as in equation (7), we minimise expected information (Morphet 1975).

The free energies which we have defined are exergies. Exergy is that component of enegy in a thermodynamic system, which is capable of useful work. Thus in minimising free energy we are minimising the maximum available work energy. In looking for efficiency in energy use we should look to identify and exploit that exergy which remains available after a process has completed (Fisk, 2006). Simply looking at energy efficiency is less illuminating because energy is always conserved, whereas exergy is used, and used up, in the performance of work.. Thus in the singly constrained model we may interpret equation (25) as identifying the useful work done as *U-TS* reflecting the fact that the entropy times the temperature is that energy which goes missing in the process. In transport terms this lost energy reflects the losses due to costs which do not directly achieve the transport purpose of converting origins into destinations. Such costs might include the costs of congestion or other forms of delay and the lack of information on the best routes available. Efficiency would be gained by reducing entropy and by using that exergy remaining after the transfer of origins into destinations.

[4] Tribus and McIrvine use a different formulation for information, namely the differential entropy. This is explored in Appendix 2.

9. System Dynamics

The model as defined in equation (20), makes no reference to time although, as was argued in the case of the additional constraint on total trips, this information is in part, implied within the data which normally refer to a period of time over which trips were sampled, e.g. peak hour, 24 hour. However, even given this period there is no information within the model about the rate of transfer of origins into destinations; this could be instantaneous or it could be distributed over the sample period. In reality, although estimated simultaneously the balance of origins and destinations does not exist simultaneously but rather at any one time, the progressive evacuation of the origin zones is balanced by the trips in transit and those trip ends which now occupy the destination zones. The decomposition of free energy demonstrated in the preceding section suggests that it may be a useful characterisation of the position of the system at an instant in the time period for the conversion of origins into destinations and the understanding of the model in continuous terms. However, the conversion of origins into destinations is not the only aspect of dynamic change although it may be the most easily observed. We need also to look at changes that may result from changing temperatures i.e. changing β values. This is done in the next section where we identify phase changes in the system reflecting changes in the balancing factors. In the case of the origin and destination constrained model these changes are hidden as changes within the A_i and B_j values. However, when the A_i and B_j values are fixed the changes evidence themselves as changes in the distribution of origin and destination values.

10. Exploring Specific Heat and Phase Change

The definition of specific heat ,ζ , is given by

$$\frac{\partial U}{\partial T} = \zeta \tag{76}$$

but $T = \frac{1}{\beta}$ and we may write

$$\frac{\partial \beta}{\partial T} = -\frac{1}{T^2} \tag{77}$$

and therefore

$$\frac{\partial U}{\partial T} = -\frac{1}{T^2}\frac{\partial U}{\partial \beta} = -\beta^2 \frac{\partial U}{\partial \beta} \tag{78}$$

The expression for internal energy is, for the unconstrained case

$$U = \sum_i \sum_j p_{ij} c_{ij} = \frac{1}{\sum_i \sum_j e^{-\beta c_{ij}}} \sum_i \sum_j c_{ij} e^{-\beta c_{ij}} \tag{79}$$

so we may write

$$\frac{\partial U}{\partial \beta} = -\frac{\sum_i \sum_j c_{ij}^2 e^{-\beta c_{ij}}}{Z_u} + \frac{\left(\sum_i \sum_j c_{ij} e^{-\beta c_{ij}}\right)\left(\sum_i \sum_j c_{ij} e^{-\beta c_{ij}}\right)}{Z_u^2}. \tag{80}$$

and therefore

$$\frac{\partial U}{\partial T} = -\beta^2 \frac{\partial U}{\partial \beta} = \beta^2 \left(\left\langle c_{ij}^2 \right\rangle - \left\langle c_{ij} \right\rangle^2 \right) \tag{81}$$

so the specific heat is β^2 times the variance of the energy. This result is similar to that from standard statistical mechanics (Sethna, 2008) and is consistent with the formulation of specific heat as

$$\zeta = \beta^2 \frac{\partial^2 \ln Z}{\partial \beta^2} \tag{82}$$

but contains no information as to what is held constant. Given that we have neither pressure nor volume it is reasonable to ask to what is the specific heat specific? In this case it is specific to the trip and the total number of trips is what is held constant. What distinguishes the unconstrained and the constrained models is their differing formulation of p_{ij}. and the use of the cost definition of equation (35) in the case of the doubly constrained model. Effectively we are using enthalpy, *H*, as defined in equation (55) rather than internal energy, a standard approach in thermodynamics. Diagrams 2 and 5 below show the variation of specific heat with $\frac{1}{\beta}$ for the unconstrained and doubly constrained models with, as might be expected a higher specific heat in the doubly constrained case where work is being done, through the balancing factors, against the constraints. As temperature rises in both cases a limit is approached, of zero in the case of the unconstrained model. In the case of the constrained model a positive limit is approached consistent with the effect of the constraints which prevent the temperature rise increasing entropy to a maximum. In both cases there is a turning point in specific heat at a critical temperature, T_c. This and the shape of the curves are consistent with there being a phase change at T_c. Comparison with similar diagrams for gases (Fisher,1964 reproduced in Yeomans, 1992) offers some verification. Diagram 3 plots the data against $\frac{T}{T_c}$ consistent with the Fisher and Yeomans presentation. Diagram 2 shows two estimates of specific heat, that of equation (81) and that of the more basic interval definition, $\frac{\Delta U}{\Delta T}$. The fit is very close and the interval definition (in this case $\frac{\Delta H}{\Delta T}$) is used in diagram 5. The use of specific heat to identify phase change is considerably clearer than the use of free energy where the kink at low temperature shown in Diagram 1 is less than distinct. Diagram 4 shows what is happening to the unconstrained origins as the temperature rises. The rise and fall takes place on either side of the critical temperature suggesting a zone of instability. The same analysis is not available in the constrained case as the origins are, by definition, fixed. However, Diagram 6 shows a similar analysis for the accessibility constrained model with the A_i and B_j of equation (A3.5) held constant. The equation is reproduced below as equation (83).

$$T_{ij} = \frac{A_i B_j}{k} \frac{O_i D_j}{N} e^{-\beta c_{ij}} \quad (83)$$

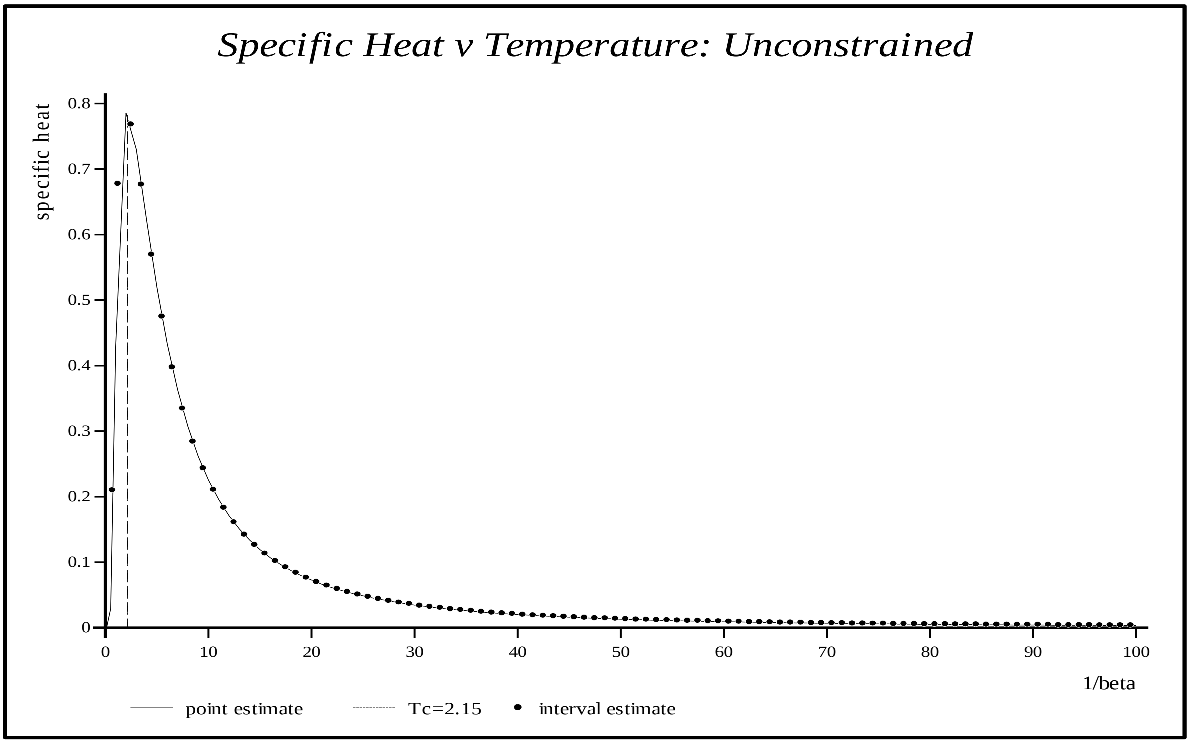


Diagram 2

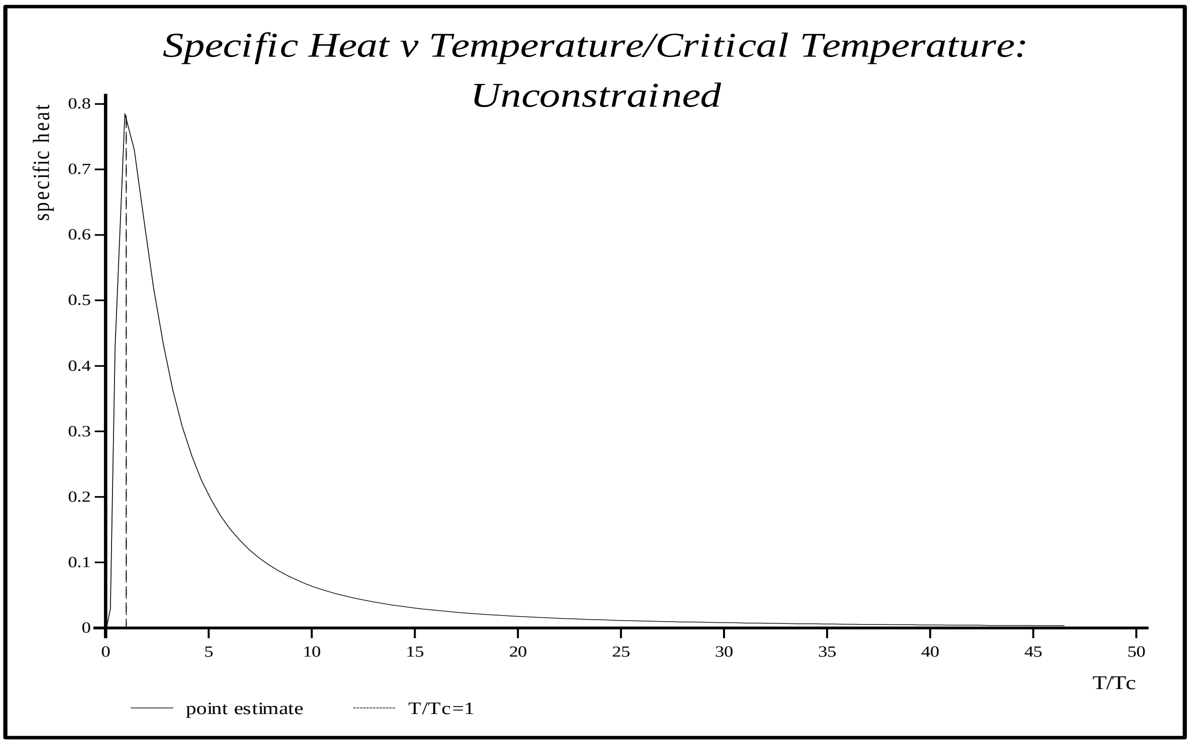


Diagram 3

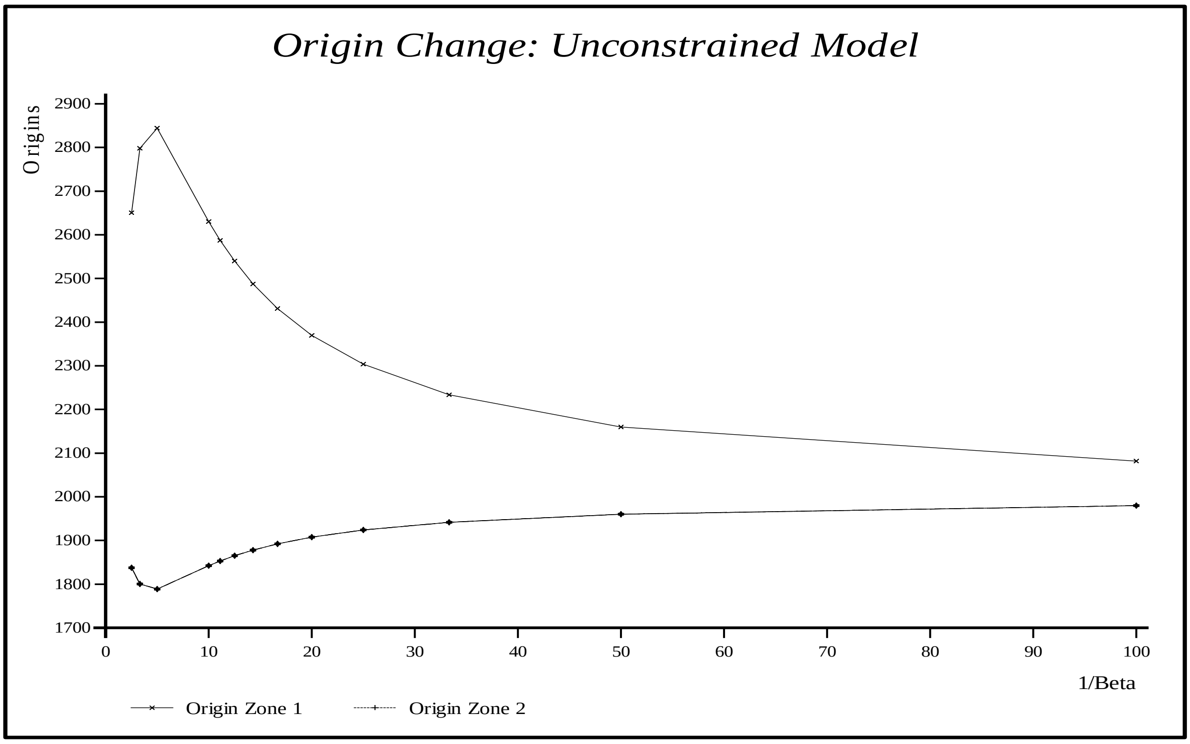


Diagram 4

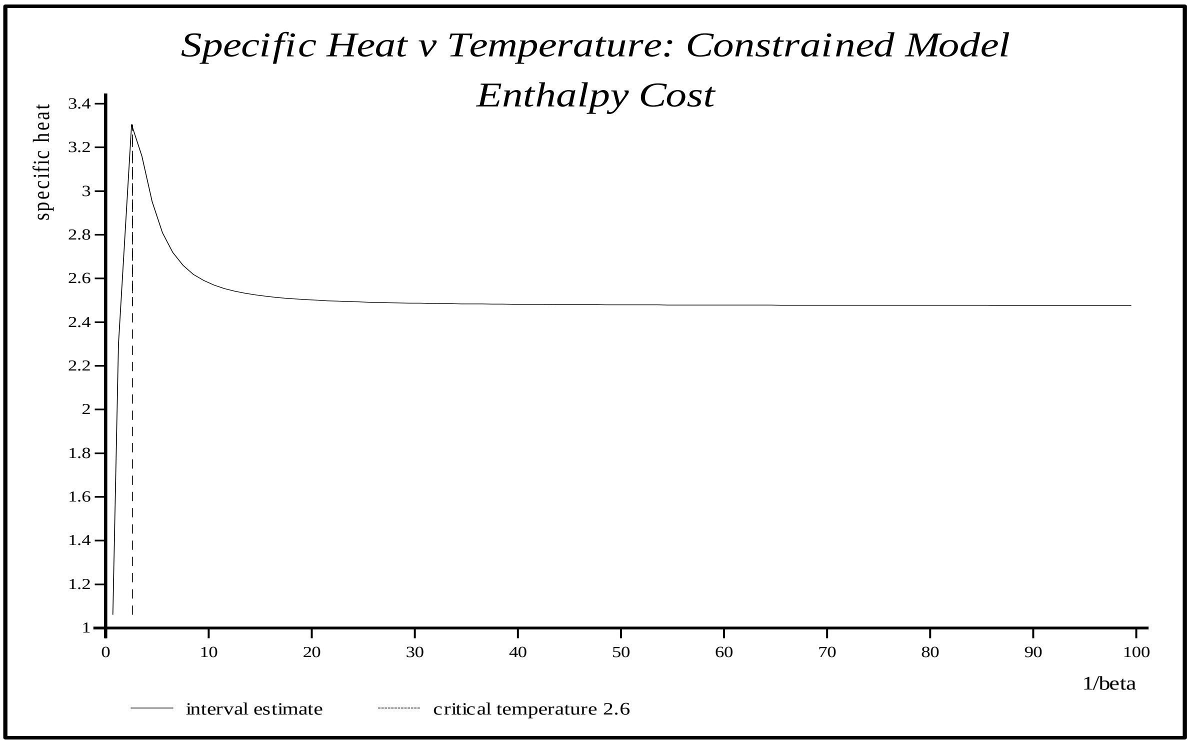


Diagram 5

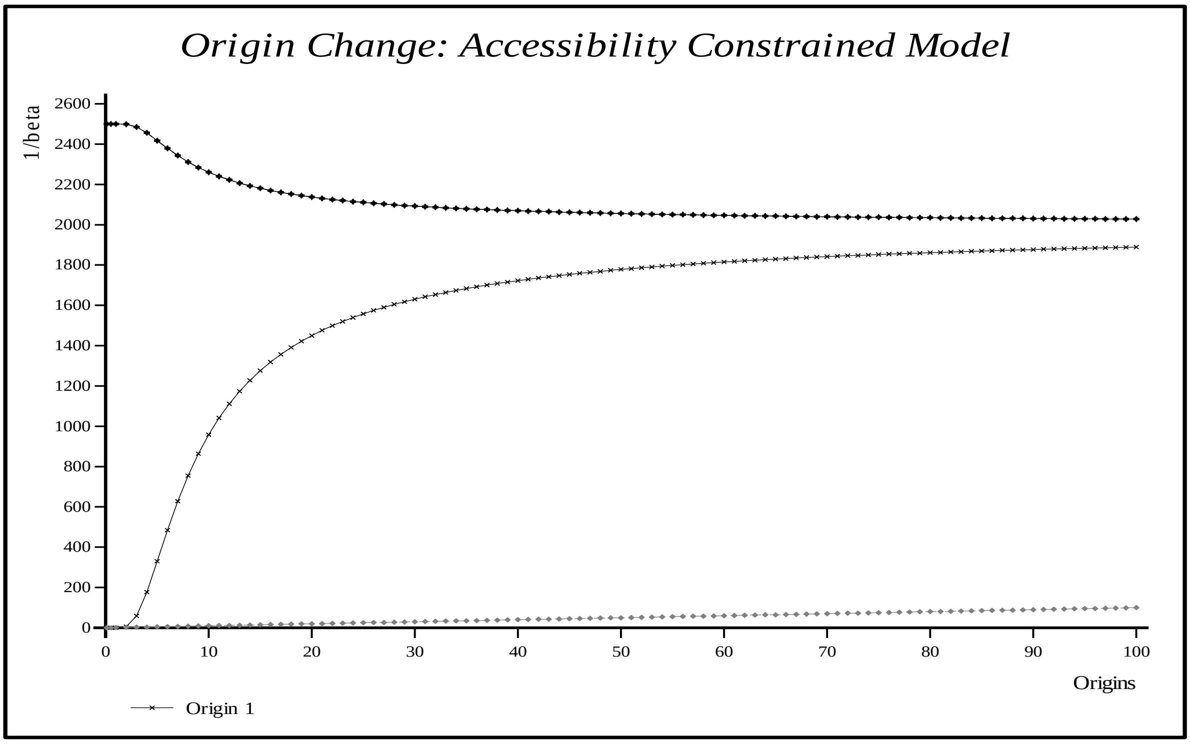


Diagram 6

It indicates that the model is symmetrical between O_i and D_j and A_i and B_j so that we can iterate to fixed pressures (i.e. balancing factors) allowing trip ends to vary subject to their adding up to *N*. It might be argued that, unlike the case of origins and destinations, we do not have any *a priori* values for the balancing factors with which to constrain the iteration. However, we do have the choice of either iterating to previously determined balancing factors whilst changing some other parameter e.g. c_{ij}. Alternatively, we might argue that in the longer term the factors might be expected to equalise since they represent accessibilities which at equality would give a Pareto optimum. It has been argued (Tribus and Evans, 1970) that the Langrage multipliers relating to subsystems will tend to equality across the system as a whole. Knowing that accessibility is equal system wide we can iterate to any convenient constant value with the normalization to *N* ensuring the validity of the result.. This version of the model gives an explicit link between change in the model parameters and change in land use as exemplified by the changes in the origins and destinations.

The zone of instability around the critical value of $\frac{1}{\beta}$ may include within it the potential values of β in the calibrated model. In such circumstances the calibration search may prove difficult both because the search path may cross phases and because if, in reality, phase change is incipient then a single equilibrium model may be inappropriate and a different modelling strategy may be required.

11. Interpretation

The daily commuting flow of traffic might be seen as reflecting the cyclic compression and expansion of an ideal gas in a heat engine as in a Carnot cycle (Fisk, 2006) . In the doubly constrained model the initial isothermal expansion determines the origins and the subsequent expansion, the destinations. The work done and energy dissipated is replaced by the heat bath maintaining the isothermal nature of the process. The analysis takes no account of the value of the destinations achieved just as the thermodynamic analysis of the heat engine takes no account of the purpose and value of the work produced.
This approach looks at the work done in terms of the pressure and volume work defined in conventional thermodynamic analysis. However, thermodynamics can include many other energies, eg magnetic and electric and we may consider the energy associated with the origins and destinations as being a particular land use transport energy inherent in the pattern of trips and trip ends.

We have identified β with the inverse of temperature which, even in classical thermodynamics, is true only for an ideal dilute, monatomic gas. It would seem better to interpret β as a modulus converting energy to information and vice versa. This is closer to Gibbs original view (Gibbs, 1902) and clarifies the role of entropy as missing or inaccessible information (Ben-Naim, 2008) so that we may interpret $-\frac{1}{\beta}\sum_i\sum_j p_{ij}\ln p_{ij}$ as inaccessible energy. It remains to interpret β in land use transport terms where it would seem to represent a measure of the efficiency of the use of information in directing the use of those resources identified in the definition of generalised cost. Temperature $1/\beta$, has been interpreted as measuring the level of economic development, (Saslow, 1999) and we might therefore expect to interpret $1/\beta$ as an index of the level of development of the system under consideration with such efficiency being higher in developed economies.

12. Conclusions

In this paper we have identified the partition function corresponding to the maximum entropy trip distribution model. From this has followed a definition of the free energy which, in the case of the unconstrained model, corresponds to Helmholtz free energy. The constrained model gives free energies more closely corresponding to Gibbs or Landau free energies. However we have shown that the free energy, of whatever form, is closely related to expected information and that minimising free energy is equivalent to minimising expected information which gives a similar model derivation to that of entropy maximisation. In fact Evans (Evans, 1978) argues that information minimisation is more general as it admits of constraints that are not linear in p_{ij}, unlike entropy maximisation.

The generalised free energy expressed in the terms of a land use model opens up the possibility of an explicitly spatial exergy analysis of land use patterns.

The decomposition of free energy gives some insight into the dynamics of the system as it transfers origins to destinations whilst the derivation of an expression for specific heat gives a useful mechanism for comparing city transport systems since it is a dimensionless ratio unlike β . The specific heat measure is also seen to be an effective indicator for phase change as β changes.

The location of the analysis in an economic framework may be desirable but will require the relating of economic measures to those of thermodynamics. Thus free energy may be related to value (Friston,2007), or to wealth (Saslow, 1999).

Several questions still remain. The trips/particles have been treated as distinguishable but in fact we can only distinguish between trips that go between differing origin or destination zones. Within an interchange ij the trips T_{ij} are indistinguishable with common energy levels. This and the fact that the energy levels or zone to zone travel costs are not continuous, suggest that using the mathematical apparatus of quantum analysis might produce some useful insights and confirm or otherwise, the classical analysis used here.

Although we have leant heavily on statistical mechanics and thermodynamics to guide the exploration in this paper it would be well to bear in mind Jaynes' view that 'statistical mechanics is a branch of inference'. We might therefore seek to develop future work in this area as inference applied to land-use transportation systems and seek to identify further information that might be included in the constraints.

Appendix 1

A1. Test Data

In the following calculations[5] we consider a cost matrix

10	14.1	14.1	14.1	14.1
14.1	10	20	28.3	20
14.1	20	10	20	28.3
14.1	28.3	20	10	20
14.1	20	28.3	20	10

with $\beta = 0.1$ giving the deterrence function matrix is

0.3678794412	0.2441432832	0.2441432832	0.2441432832	0.2441432832
0.2441432832	0.3678794412	0.1353352832	0.05901285367	0.1353352832
0.2441432832	0.1353352832	0.3678794412	0.1353352832	0.05901285367
0.2441432832	0.05901285367	0.1353352832	0.3678794412	0.1353352832
0.2441432832	0.1353352832	0.05901285367	0.1353352832	0.3678794412

In the case of the constrained models we assume origins and destination.
The origins (row totals) are

500 500 3000 5000 1000

and the destinations (column totals) are

5000 3000 1000 500 500

The total number of trips is 10,000.

A2. The Unconstrained Case

In the unconstrained case (i.e. not using the Origin and Destination totals) the trip matrix is (rounding to integers)

720	478	478	478	478
478	720	265	115	265
478	265	720	265	115
478	115	265	720	265

[5]Calculations in Dyalog APL 12.0.5 incorporating Causeway RainPro graphics

478	265	115	265	720

and hence the p_{ij} matrix is (to 8 decimal places)

0.07197407	0.04776561	0.04776561	0.04776561	0.04776561
0.04776561	0.07197407	0.02647778	0.01154562	0.02647778
0.04776561	0.02647778	0.07197407	0.02647778	0.01154562
0.04776561	0.01154562	0.02647778	0.07197407	0.02647778
0.04776561	0.02647778	0.01154562	0.02647778	0.07197407

This gives an entropy $S = -\sum_i \sum_j p_{ij} \ln p_{ij} =$ 3.084456695

And an average cost ($U = \bar{C} = \sum_i \sum_j p_{ij} c_{ij}$) of 14.53007

And a value

$$Z_u = \sum_i \sum_j e^{-\beta c_{ij}} = 5.111277152 \qquad \text{(A1.1)}$$

giving a free energy $F = -\frac{1}{\beta} \ln Z$ = -16.31449305

We may now calculate independently, from A1 and A2, the value of the expression

$$U - \frac{1}{\beta} S = \text{-}16.31449305$$

thus demonstrating the validity of the derivation in the unconstrained case.

A3. The Doubly Constrained Case

In the constrained case, with β = 0.1, we iterate the deterrence matrix to the given origin and destination totals to get a trip matrix of

215	211	37	13	25
143	319	20	3	14
1305	1069	505	66	56
2882	1029	410	395	283
455	372	28	23	122

leading to a probability matrix of

0.02146974	0.02105062	0.00365735	0.00129634	0.00252594
0.01433188	0.03190530	0.00203925	0.00031518	0.00140840
0.13048999	0.10686671	0.05047063	0.00658108	0.00559161

0.28822429 0.10292749 0.04101074 0.03951347 0.02832400
0.04548411 0.03724988 0.00282203 0.00229393 0.01215005

from which we can extract balancing factors using the formulation of Kirby that these factors ,corresponding to the r_i and s_j of equation(20) giving an $r_i s_j$ matrix of

0.353663	0.522503	0.090780	0.032177	0.062697
0.355735	0.525564	0.091312	0.032365	0.063064
3.238923	4.785195	0.831384	0.294683	0.574194
7.154085	10.569466	1.836347	0.650890	1.268270
1.128972	1.667947	0.289790	0.102716	0.200143

and $< ln\, r_i s_j > = \sum\sum p_{ij} \ln r_i s_j = 1.0196$

From equation (11) we may calculate Z_c

$$Z = \sum_i \sum_j r_i s_j e^{-\beta c_{ij}} = 6.0599$$

In this case the entropy is given by $S = -\sum_i \sum_j p_{ij} \ln p_{ij} = 2.420065$

And the energy U by $U = \bar{C} = \sum_i \sum_j p_{ij} c_{ij} = 16.37999854$

Thus $U - \frac{1}{\beta} S =$ -7.820651

And $F = < \ln r_i s_j > - \frac{1}{\beta} \ln Z = {}^{-}7.820651$

Once again the equations balance thus verifying the derivation of free energy in the doubly constrained case.
Similarly

$$\frac{1}{\beta} I - \ln Z_u = -7.820651 \qquad \text{(A1.2)}$$

showing the equivalence of the expected information expression to free energy.

In addition

$$\sum_i \sum_j r_i s_j = 36.722866 \qquad \text{(A1.3)}$$

and

$$Z^2 = 36.722866 \qquad \text{(A1.4)}$$

illustrating that $Z^2 = \sum_i \sum_j r_i s_j$

A4. The Doubly Constrained as a Singly Constrained Case

In this model we examine the singly constrained case in which the balancing factors r_i, s_j are incorporated into the cost matrix and thus into the probability matrix.

The probability matrix is given by

0.02146974	0.02105062	0.00365735	0.00129634	0.00252594
0.01433188	0.03190530	0.00203925	0.00031518	0.00140840
0.13048999	0.10686671	0.05047063	0.00658108	0.00559161
0.28822429	0.10292749	0.04101074	0.03951347	0.02832400
0.04548411	0.03724988	0.00282203	0.00229393	0.01215005

which is identical to that in the doubly constrained case but the cost matrix is now

20.39	20.59	38.09	48.47	41.79
24.44	16.43	43.93	62.61	47.64
2.35	4.34	11.85	32.22	33.85
−5.58	4.72	13.92	14.29	17.62
12.89	14.88	40.69	42.76	26.09

which is considerably different from that of the doubly constrained model.. The negative value reflects the disproportionately high number of origins in zone 4. Effectively, to achieve that distribution a subsidy in excess of the transport cost is required..

The overall energy $U - \frac{1}{\beta}S$ is −18.016998 which compares with $U - \frac{1}{\beta}S$ for the doubly constrained model of −7.8207. The difference of −10.196298 is equal to the value of $\frac{1}{\beta}\langle \ln rs \rangle$ in the doubly constrained model, as expected. The average energy of 6.183652 compares with the equivalent value in the in the doubly constrained case of 16.3800 reflecting the high impact of the subsidy on the largest trip volume. The value of Z in this case is 6.059939, the same as in the conventionally doubly constrained model.

A5. The Uniform Balancing Factor Case

In this approach the cost matrix is iterated to equal totals and the balancing factors extracted and normalised to the total number of trips giving the model

$$p_{ij} = \frac{p_{i*} . p_{*j} . e^{-\beta c_{ij}}}{Z_c} \qquad \text{(A1.5)}$$

The results for this model with the same cost and β values as before are an energy value U of 15.1466 and entropy, S of 2.9720 giving $U - \frac{1}{\beta} S$ equal to $^{-}$14.5737. From this is subtracted the value of $\frac{1}{\beta}\langle \ln rs \rangle$ of 2.332 to give -16.9057 which compares with the calculated value of $-\frac{1}{\beta} \ln Z_c$ of $^{-}$16.9058. The values of internal energy, free energy and entropy lie between those of the unconstrained and doubly constrained models as might be expected given that the constraints are stronger than the former but weaker than the latter. The trip matrix is given by

98	215	215	215	215
215	1078	397	173	397
215	397	1078	397	173
215	173	397	1078	397
215	397	173	397	1078

and has a symmetry similar to that of the unconstrained case as might be expected since the deterrence matrix determines both.

The origin (row) totals are

959 2260 2260 2260 2260

and the destination (column) totals are

959 2260 2260 2260 2260

Appendix 2

The Relation between Relative Entropy and Differential Entropy

Both differential and relative entropy are described as Expected Information and we demonstrate their relationship below.

Differential entropy, D, is defined as

$$D = S_u - S_c \tag{A2.1}$$

and relative entropy R, as

$$R = \sum_i \sum_j p_{ij} \ln \frac{p_{ij}}{q_{ij}} \tag{A2.2}$$

where the subscripts *c* and *u* refer to the constrained and unconstrained case respectively as do the probabilities p_{ij} and q_{ij}. The unconstrained case acts as our reference case.

We look first at the differential entropy and consider the constrained case in which the row and column constraints are incorporated into the cost matrix. We may write

$$U_c - \frac{1}{\beta} S_c = F \tag{A2.3}$$

That is the constrained internal energy less the constrained entropy times 'temperature' equals the free energy.
Similarly,

$$U_u - \frac{1}{\beta} S_u = A \tag{A2.4}$$

where A is the Helmholtz free energy of the unconstrained model and thus

$$U_c - \frac{1}{\beta} S_c - (U_u - \frac{1}{\beta} S_u) = F - A \tag{A2.5}$$

and so

$$\frac{1}{\beta}\left(S_u - S_c\right) = F - A - \left(U_c - U_u\right) \quad \text{(A2.6)}$$

The term $\frac{1}{\beta}\left(S_u - S_c\right)$ is the expression for information difference used by Tribus, (Tribus and McIrvine, 1971)

Now let us consider the relative entropy or expected information

$$I(p,q) = \sum_i \sum_j p_{ij} \ln \frac{p_{ij}}{q_{ij}} = \sum_i \sum_j p_{ij} \left(-\lambda_i - \lambda_j - \beta c_{ij} - Z_c + \beta c_{ij} + Z_u\right) \quad \text{(A2.7)}$$

so we may write

$$\frac{1}{\beta} I\left(p,q\right) = \frac{1}{\beta} \sum \sum p_{ij} \left(-\lambda_i - \lambda_j\right) - \frac{1}{\beta} \frac{Z_c}{Z_u} \quad \text{(A2.8)}$$

and hence

$$\frac{1}{\beta} I\left(p,q\right) = \frac{1}{\beta} \left\langle \ln r_i s_j \right\rangle + F - A \quad \text{(A2.9)}$$

The equivalence now depends upon whether or not the difference in energies is equal to $-\frac{1}{\beta}\left\langle \ln r_i s_j \right\rangle$. In general this is not the case unless either $r_i = s_j = 1$ as in the unconstrained model or $r_i = \frac{1}{s_j}$ which may be a case worth further examination. Where it is not the case recourse is had to renormalisation, to ensure that the two entropies S_u and S_c are compared at equivalent energy levels. This requires that they satisfy the equation

$$\sum_i \sum_j p_{ij} \ln q_{ij} = \sum_i \sum_j q_{ij}^{\#} \ln q_{ij} \quad \text{(A2.10)}$$

where $q_{ij}^{\#}$ is the renormalized version of q_{ij} using the escort distribution

$$q_{ij}^{\#} = C\left(q_{ij}\right)^{\alpha} \quad \text{(A2.11)}$$

where α is chosen to comply with equation (A2.10) and C is a normalising constant. (Quiroga et al, 2000). It then follows that

$$\frac{1}{\beta}\left(S_u - S_c\right) = \frac{1}{\beta} \sum_i \sum_j p_{ij} \ln \frac{p_{ij}}{q_{ij}^{\#}} = \frac{1}{\beta} \sum_i \sum_j p_{ij} \ln \frac{p_{ij}}{q_{ij}} - \frac{1}{\beta} \sum_i \sum_j q_{ij}^{\#} \ln \frac{q_{ij}^{\#}}{q_{ij}} \quad \text{(A2.12)}$$

and we see that the Tribus expression is equivalent to the expected information based on p_{ij} and q_{ij} less the expected information based on $q_{ij}^{\#}$ and q_{ij} so

$$D = I(p,q) - I(q^{\#},q) \qquad \text{(A2.13)}$$

The renormalisation may be viewed in a more familiar light, as a calibration. In calibration as in renormalisation, we assume a value for β the information energy modulus, and amend it iteratively to achieve equality in mean energy or trip length between the model and the prior or survey, data. However, a new value of β implies a new temperature or information energy modulus which does not fit with our canonical analysis in this paper in which the equilibrium is determined by a constant temperature and changes in temperature imply a new equilibrium. The usefulness of *D* is in measuring the degree of self organisation in a system (Saparin et al, 1994) but *I* is of more value in measuring actual energy changes which is what we are interested in in this case. The estimation of the destination exponent in retail models also parallels the renormalisation process.

The equivalence of free energy and the differential entropy, given constant energy, may be shown by considering equations (A2.3) and (A2.4) which may in terms of our models, be written as

$$U_c - \frac{1}{\beta}\sum_i\sum_j p_{ij}\ln p_{ij} = F \qquad \text{(A2.14)}$$

and

$$U_u - \frac{1}{\beta}\sum_i\sum_j q_{ij}\ln q_{ij} = A \qquad \text{(A2.15)}$$

so

$$U_c - U_u - \frac{1}{\beta}\sum_i\sum_j p_{ij}\ln p_{ij} + \frac{1}{\beta}\sum_i\sum_j q_{ij}\ln q_{ij} = F - A \qquad \text{(A2.16)}$$

but

$$U_c - U_u = 0 \qquad \text{(A2.17)}$$

for equal energy and therefore

$$\frac{1}{\beta}(S_u - S_c) = F - A \qquad \text{(A2.18)}$$

which proves the result.

The diagram below shows for the unconstrained model, the convergence of the two functions, $I(p,q)$ and *D*, as the value of temperature, $\frac{1}{\beta}$, rises. Convergence takes place at a value of β of approximately 0.135 . In general most calibrations are likely to give values of β locating the model in the divergent area (Department for Transport 2006, Appendix 2).

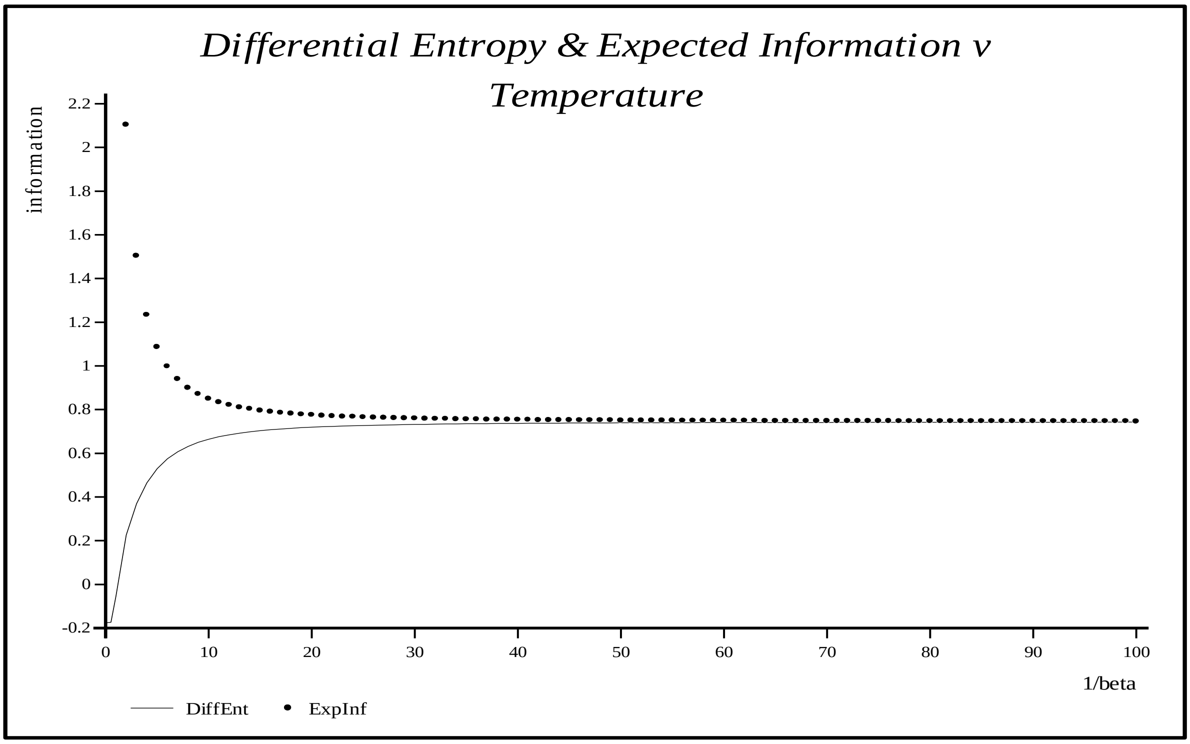

Differential Entropy & Expected Information v Temperature
information
2.2
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
-0.2
0
10
20
30
40
50
60
70
80
90
100
1/beta
DiffEnt
ExpInf

Diagram7

Appendix 3

An expression for the balancing factors

This appendix summarises the approach of Kirby (Kirby, 1970).
Consider the trip matrix with a deterrence function of *1*. This will give

$$T_{ij} = \frac{O_i D_j}{N} = \frac{\sum_j T_{ij} . \sum_i T_{ij}}{\sum_i \sum_j T_{ij}} \qquad \text{(A3.1)}$$

This is an identity in that any given T_{ij} matrix may be expressed in the manner of the right hand side of equation (A3.1). However, if we now introduce a deterrence function that varies across T_{ij}, in our case, an exponential function, we have

$$T_{ij} = \frac{O_i D_j}{N} e^{-\beta c_{ij}} \qquad \text{(A3.2)}$$

and this, in general will not balance to O_i and D_j leading to the introduction of balancing factors.

$$T_{ij} = \frac{A_i O_i B_j D_j}{N} e^{-\beta c_{ij}}$$

(A3.3)

In practice the N term is absorbed into the balancing factors giving the usual formulation

$$T_{ij} = A_i O_i B_j D_j e^{-\beta c_{ij}}$$

(A3.4)

However, Kirby, rather than accepting this absorption, introduces a new area wide balancing factor *k* thus

$$T_{ij} = \frac{A_i B_j}{k} \frac{O_i D_j}{N} e^{-\beta c_{ij}}$$

(A3.5)

This relation may be rewritten as

$$\frac{T_{ij}}{e^{-\beta c_{ij}}} = \frac{A_i B_j}{k} \frac{O_i D_j}{N}$$

(A3.6)

which is now in the same form as equation A4.1 so we may write

$$\frac{T_{ij}}{e^{-\beta c_{ij}}} = \frac{\sum_j \frac{T_{ij}}{e^{-\beta c_{ij}}} . \sum_i \frac{T_{ij}}{e^{-\beta c_{ij}}}}{\sum_i \sum_j \frac{T_{ij}}{e^{-\beta c_{ij}}}} \qquad \text{(A3.7)}$$

or

$$T_{ij} = \frac{\sum_j \frac{T_{ij}}{e^{-\beta c_{ij}}} . \sum_i \frac{T_{ij}}{e^{-\beta c_{ij}}}}{\sum_i \sum_j \frac{T_{ij}}{e^{-\beta c_{ij}}}} e^{-\beta c_{ij}} \qquad \text{(A3.8)}$$

For the single particle case we may write this as

$$\frac{p_{ij}}{e^{-\beta c_{ij}}} = \frac{\sum_i \frac{p_{ij}}{e^{-\beta c_{ij}}} . \sum_j \frac{p_{ij}}{e^{-\beta c_{ij}}}}{\sum_i \sum_j \frac{p_{ij}}{e^{-\beta c_{ij}}}} = \frac{r_i s_j}{Z_c} \qquad \text{(A3.9)}$$

This identity may be expressed in a number of ways. In particular we may write

$$\frac{p_{ij}}{q_{ij}} = \frac{\sum_j \frac{p_{ij}}{q_{ij}} \sum_i \frac{p_{ij}}{q_{ij}}.}{\sum_i \sum_j \frac{p_{ij}}{q_{ij}}} \qquad \text{(A3.10)}$$

where $q_{ij} = \frac{e^{-\beta c_{ij}}}{\sum_i \sum_j e^{-\beta c_{ij}}}$

From equation (A3.9) we may write

$$Z_c = \sum_i \sum_j \frac{p_{ij}}{e^{-\beta c_{ij}}} \qquad \text{(A3.11)}$$

from 1.1

$$\sum_i \sum_j \frac{p_{ij}}{e^{-\beta c_{ij}}} = \sum_i \sum_j \frac{r_i s_j}{Z_c} \qquad \text{(A3.12)}$$

therefore

$$Z_c^2 = \sum_i \sum_j r_i s_j \tag{A3.13}$$

for N particles

$$2\ln Z_c = \ln \sum \sum r_i s_j = \ln N < r_i s_j > \tag{A3.14}$$

So for a single particle

$$2\ln Z_c = \ln < r_i s_j > \tag{A3.15}$$

We may also write, using equation (A3.9) and summing over *j*.

$$Z_c \sum_j \frac{p_{ij}}{e^{-\beta c_{ij}}} = Z_c r_i = \sum_j r_i s_j = r_i \sum_j s_j \tag{A3.16}$$

and thus

$$Z_c = \sum_j s_j \tag{A3.17}$$

Similarly, summing over *i* gives

$$Z_c = \sum_i r_i \tag{A3.18}$$

Summing up we may say

$$Z_c = \sum_i r_i = \sum_j s_j \tag{A3.19}$$

and

$$Z_c^2 = \sum_i \sum_j r_i s_j = \sum_i r_i \sum_j s_j \tag{A3.20}$$

Further we may consider r_i and s_j themselves as row and column partition functions Z_i and Z_j such that

$$p_{ij} = \frac{Z_i Z_j}{Z_c} e^{-\beta c_{ij}} \tag{A3.21}$$

In the case of the unconstrained model we may write, from equation (A3.18) that

$$Z_u = \sum_i r_i = n \tag{A3.22}$$

and, summing (A3.21) over *i* and *j*

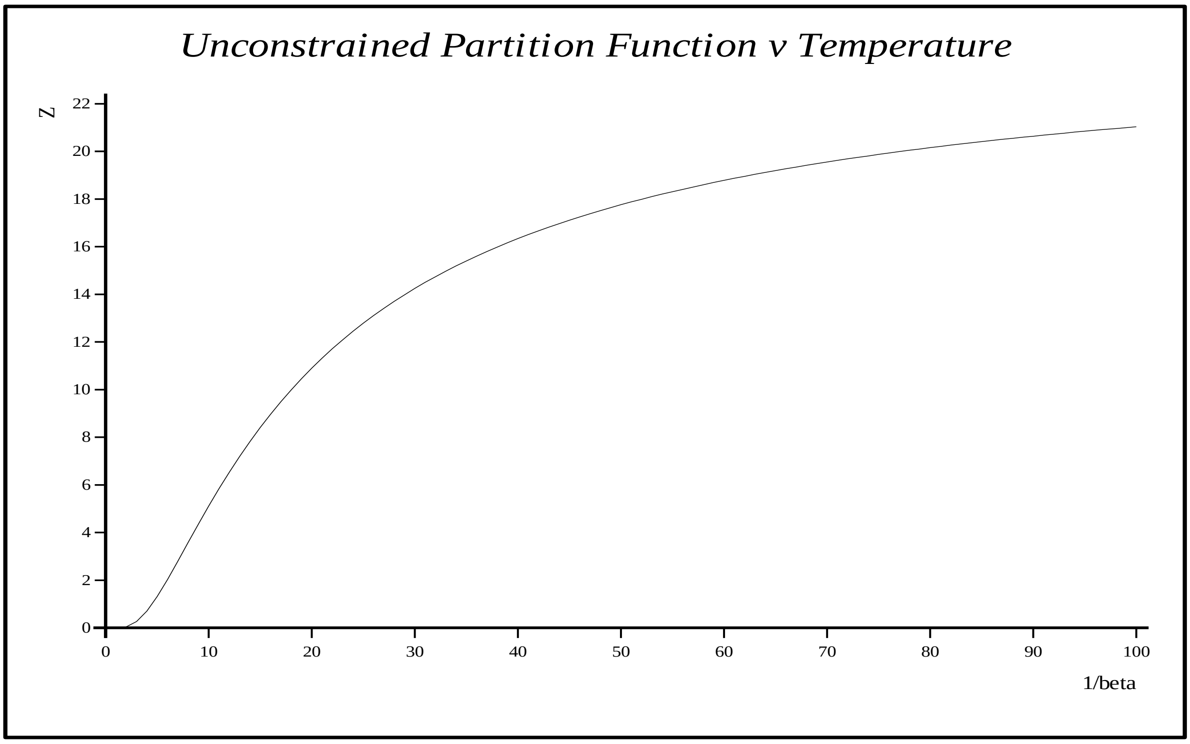
$$Z_u = \sum_i \sum_j e^{-\beta c_{ij}} \tag{A3.23}$$

In the case of the unconstrained model of Appendix 1 A2 the value of *n* is 5 but we see from equation (A1.1) that Z_u has a value of 5.111277152. This discrepancy arises from the biproportionality already inherent in the deterrence function matrix.. On the one hand this problem of deterrence biproportionality may be seen as a weakness of the biproportional model which may be reduced by amending the zoning pattern. On the other hand, the embedded biproportionality may be seen as an inherent feature of the deterrence matrix which reflects the real world system being modelled. This is likely to be true if the cost matrix includes additive row and column elements in the cost elements (prior to any consideration of terminal costs). Such costs might reflect the trip cost internal to the zone which forms part of the trip costs for all trips to or from the zone in question.

Embedded biproportionality is likely to affect calibration although not the resulting trip pattern as the biproportionality of the deterrence matrix will be absorbed by the overall doubly constrained iteration into its balancing factors. However, since the calibrated function would be $e^{-\gamma_i-\gamma_j-\beta c_{ij}}$ where β is the true value and γ_i, γ_j are the pre-existing biproportionality factors, the incorrect estimation of β would affect those applications where its value is required. This would be true for values of free energy and for some calculations of elasticity. An estimation of the true value of β may be gained from the solution of equations (A3.22) and (A3.23).

The low value of Z_u may also relate to the low temperature behaviour eliminating some origins and destinations and as a consequence, destroying the underlying symmetry of the original model.

Diagram 8 shows how, for the data of Appendix 1, the value of Z_u approaches n^2 as β decreases, i.e. as temperature increases. The divergence from n^2 starts at a value for of about 0.04 and increases as β increases into the range of values we might normally expect in a transport model (Department for Transport,2006). A similar analysis applies when working from equation (A3.10) rather than equation (A3.9) but the values for r_i, s_j and Z_c will differ reflecting the fact that equation (A3.9) refers to an iteration from $e^{-\beta c_{ij}}$ and equation (A3.10) to an iteration from q_{ij}. The two iterations determine two different reference environments and will accordingly, give different free energy values by a factor proportional to Z_u. The use of a reference environment means that in looking at changes in the system the effect of embedded biproportionality will not be very important.


Unconstrained Partition Function v Temperature
Z
22
20
18
16
14
12
10
8
6
4
2
0
0
10
20
30
40
50
60
70
80
90
100
1/beta
Diagram 8

Appendix 4

The Decomposition of Expected Information

Expected Information, I, is given by

$$I = \sum_i p_{ij} \ln \frac{p_{ij}}{q_{ij}} \tag{A4.1}$$

where p_{ij} is the posterior distribution and q_{ij} is the prior. In thermodynamic terms $\frac{1}{\beta} I$ is the change in potential defined by the prior and posterior states of the system.

We may write

$$\sum_i \sum_j p_{ij} \ln \frac{p_{ij}}{q_j} = \sum_i p_{i*} \sum_j \frac{p_{ij}}{p_{i*}} \left[\ln \frac{\frac{p_{ij}}{p_{i*}}}{\frac{q_{ij}}{q_{i*}}} + \ln \frac{p_{i*}}{q_{i*}} \right] = \left[\sum_i p_{i*} \sum_j \frac{p_{ij}}{p_{i*}} \ln \frac{\frac{p_{ij}}{p_{i*}}}{\frac{q_{ij}}{q_{i*}}} \right] + \sum_i p_{i*} \ln \frac{p_{i*}}{q_{i*}}$$

$$= \sum_i p_{i*} I_i + \sum_i I_{O_i} \tag{A4.2}$$

where

$$p_{i*} = \sum_j p_{ij} \tag{A4.3}$$

and

$$q_{i*} = \sum_j q_{ij} \tag{A4.4}$$

I_i is the expected information calculated across j for row i and I_{O_i} is the expected information associated with the row (origin) total.

We may thus write

$$I = \sum_i \left(p_{i*} I_i + I_{O_i} \right) = \sum_j \left(p_{*j} I_j + I_{D_j} \right) \tag{A4.5}$$

This decomposition is based on Theil (Theil, 1967, Theil 1972) and suggests an interpretation of I_i as a within row effect and and I_{O_i} as a between row effect. A similar decomposition may be effected for free energy thus

$$F\beta = \sum_i \sum_j p_{ij} \ln \frac{p_{ij}}{e^{-\beta c_{ij}}} = \sum_i p_{i*} \sum_j \frac{p_{ij}}{p_{i*}} \left[\ln \frac{\frac{p_{ij}}{p_{i*}}}{e^{-\beta c_{ij}}} + \ln \frac{p_{i*}}{e^{-\beta c_{ij}}} \right] = \sum_i p_{i*} \sum_j \frac{p_{ij}}{p_{i*}} \left[\ln \frac{\frac{p_{ij}}{p_{i*}}}{e^{-\beta c_{ij}}} \right] + \sum_i p_{i*} \ln \frac{p_{i*}}{\sum_j e^{-\beta c_{ij}}} \tag{A4.6}$$

thus

$$F = \frac{1}{\beta}\left(I - Z\right) = \sum_i p_{i*} F_i + \frac{1}{\beta} \sum_i p_{i*} \ln \frac{p_{i*}}{Z_i} \tag{A4.7}$$

where

$$Z_i = \sum_j e^{-\beta c_{ij}} \tag{A4.8}$$

References

Ben-Naim, A., *A Farewell to Entropy: Statistical Thermodynamics Based on Information*, World Scientific, Singapore, 2008

Berry, B.J.L., *Cities as Systems Within Systems of Cities*, Papers In Regional Science 13: pp 147-164, 1964

Callen, H.B., *Thermodynamics and an Introduction to Thermostatics*, John Wiley, New York, 1985

Cowan, B., *Topics in Statistical Mechanics*, Imperial College Press, London,2005

Department for Transport, *Variable Demand Modelling – Key Processes*, TAG Unit 3.10.3, Transport Analysis Guidance, June 2006

Dieter, K.H., *Distribution of Work Trips in Toronto*, Journal of the City Planning Division, Proceedings of the American Society of Civil Engineers, CP1, pp 9-28, August 1962

Evans,A.W., *Some Properties of Trip Distribution Models*, Transportation Research, 1970, Vol. 4, pp 19 – 38

Evans, R.B., *Thermodynamic Isolation and Essergy Analysis*, Energy, vol.5, 1980, pp 805-821

Evans, R. B., *A New Approach for Deciding upon Constraints in the Maximum Entropy Formalism*, in Levine, R.D and Tribus, M., *The Maximum Entropy Formalism*, MIT Press, 1978

Evans, R.B. and Tribus,M.,*Thermo-economics of Saline Water Conversion*, I & EC Process Design and Development, vol 4, No. 2, 1965, pp 195-206

Fisher, M.E., *Specific Heat of a Gas neat the Critical Point*, Physical Review, vol136, No.6A, 1964, pp 1599-1604

Fisk, D., *Urban Energy Systems,* in *Factor 10 Engineering for Sustainable Cities,* IABSE Henderson Colloquium, Cambridge, 10-12 July 2006

Finn, C.B.P., *Thermal Physics*, Routledge Keegan & Paul, London, 1986

Friston, K.J., Stephan, K.E., *Free Energy and the Brain*, Synthese, vol 159, 2007, pp 417-458

Gibbs, J.W., *Elementary Principles in Statistical Mechanics*, Yale University Press, 1902 reproduced by Dover, New York, 1960

Jaynes, E.T., *Information Theory and Statistical Mechanics*, Physical Review vol. 106, no. 4, 1957, pp 620-630

Jaynes, E. T., *On the Rationale of Maximum-Entropy Methods*, Proceedings of the IEEE, vol. 70, no. 9, 1982, pp 939-952

Keenan, J.H., *Thermodynamics*, 12th edn, Wiley, New York, 1956

Kirby, Howard R., *Normalizing Factors of the Gravity Model – An Interpretation*. Transportation Research, Vol. 4, pp 37-50 1970

MacDonald, D.K.C.,*Introductory Statistical Mechanics for Physicists*,Dover, Mineola, 2006

Morphet, R., *A Note on the Calculation and Calibration of Doubly Constrained Trip Distribution Models*, Transportation 4 (1): 43-53, 1975.

Quiroga, R.Q., Arnhold, J., Lehnertz, K. and Grassberger, P., *Kullback-Leibler and renormalized entropies: Applications to encephlograms of epilepsy patients*, Physical Review E, 62(6): 8380-8386, December 2000

Saparin, P., Witt, A., and Anishchenko, V., *The Renormalized Entropy-an Apprpriate Complexity Measure*, Chaos, Solitons and Fractals, 4(10), 1907-1916, 1994

Saslow, W.M., *An economic analogy to thermodynamics*, American Journal of Physics, vol. 67, no. 12, December 1999

Sethna, J.P., *Statistical Mechanics: entropy, order parameters and complexity*, Oxford University Press, Oxford, 2008

Sornette, D., *Critical Phenomena in Natural Sciences*, springer-Verlag, Berlin, 2000

Theil, H., *Economics and Information Theory*, North-Holland, Amsterdam, 1967

Theil,H., *Statistical Decomposition Analysis*, North-Holland, Amsterdam, 1972

Tribus, M., *Thermostatics and Thermodynamics*, van Nostrand, New York, 1961

Tribus, M., *Information Theory as the Basis for Thermostatics and Thermodynamics*, Journal of Applied Mechanics, pp1-8, March 1961

Tribus,M. and Evans, R.B., *A Minimal Statistical Mechanics from which Classical Thermostatics may be Derived*, A critical Review of Thermodynamics, Stuart, E. B. Gal-Or, B., and Brainard, A. J.editors, MONO BOOK Copr, Baltimore, 1970

Tribus, M. and McIrvine, E.C., *Energy and Information,* Scientific American, vol. 224, no. 3, pp179-188, 1971

Wilson, A., *The thermodynamics of the city*, Paper 137, CASA Working Papers Series, University College, London, July 2008

Wilson, A., *Entropy in urban and regional modelling*, Pion, London, 1970

Yeomans, J.M., *Statistical Mechanics of Phase Transitions*, Oxford University Press, Oxford,1992