This equation gives reasonable predictions for both gas-liquid and liquid-liquid systems. The above form of the equation is not applicable to gases like hydrogen and helium owing to quantum effects (Nakanishi et al., 1965). It is the purpose of this note to extend the above equation to quantum gases also.

It is known (Ferrell and Himmelblau, 1967) that quantum effects in diffusion are related to the square of de Boer's quantum mechanical parameter Λ^*, defined as

$$\Lambda^* = \frac{h}{\sigma (m\epsilon)^{1/2}} \qquad (2)$$

This dimensionless parameter Λ^* was devised by de Boer and co-workers (de Boer and Bird, 1964) as a measure of the quantum effects in gases and liquids.

In Table 1, the product of diffusion coefficient, D, and square of solute molecular diameter σ is shown for different gases in CCl_4, $(C_4F_9)_3N$, and water at 20°C. The quantum parameter for each gas is also listed. To relate the quantum parameter to the diffusion coefficient, we have chosen argon as a reference gas since it has a small quantum parameter. Alongside the values of $D\sigma^2$ are shown the relative values compared to argon, that is, $D\sigma^2/D\sigma^2$ for argon. It can be seen that this ratio is a constant for a given solute gas. In Figure 1 this ratio is plotted against the parameter $(1 + \Lambda^{*2})$. From this figure it can be seen that diffusion coefficients are directly related to $(1 + \Lambda^{*2})^{0.5}$. This, then, gives an indication of the magnitude of quantum effects. For example, hydrogen diffuses twice as fast as any similar sized molecules.

Thus, Equation (1) is modified to

$$D_{AB} = 0.088 \frac{V_B^{*4/3}}{N^{2/3}} \frac{RT}{\mu V_o} \frac{(1 + \Lambda^{*2})^{1/2}}{V_A^{*2/3}} \qquad (3)$$

Table 2 compares the predictions of Equation (3) with experimental data and the Akgerman-Gainer equation. This equation has been found more suitable than other equations (Akgerman and Gainer, 1972). It is seen that both equations give very similar predictions.

The Akgerman-Gainer equation uses molar volumes of the solute at their normal boiling point. The molar volume is computed in an additive fashion from individual atoms. These values differ considerably (Sovova, 1976). Equation (3) uses critical molar volumes and is more convenient to use.

The scatter in experimental data is rather large. Owing to its low solubility, the measurement of diffusivity of hydrogen is difficult. Some experimental data carry considerable error as seen from the values for cyclohexane and n-hexane. More accurate diffusion data are needed to test these theories of the liquid state. Perhaps the only way to choose among the available equations is to compare their predictions over a wide range of temperatures. Such data are, at present, unavailable.

NOTATION

D = diffusion coefficient
h = Planck's constant
m = molecular mass
N = Avogadro number
R = universal gas constant
T = temperature
V^* = critical molal volume
V_o = intrinsic molal volume = $0.31\, V_B^*$
ϵ = force constant
Λ^* = de Boer quantum parameter
μ = solvent viscosity
σ = force constant in Lennard-Jones 6-12 potential

Subscripts

A = solute
B = solvent

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Analytical Model Reduction of Large Scale Linear Dynamic Systems

A class of dynamic model approximation techniques based on a frequency domain Taylor series expansion is presented. These methods yield low-order models and are analytical rather than computational in nature; that is, one can retain important parameters (which may be time varying) from the original model in functional form in the low-order model. This feature is very attractive for on-line updating of the simplified model and subsequent control of the process. An example for a tenth-order original model has shown that the analytical low-order models provide excellent approximations to the step response of the original system.

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The physical models for reaction, separation, and heat exchange processes exhibit a rather strong dependence upon parameters which may vary during operation. For example, variations in flow rate influence the residence time of the above processes and thus have a significant effect on the system dynamics. High performance control

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of these systems demands updating of the model parameters by filtering the output data or by direct measurement when possible. Control algorithms can then be implemented based on the new model. However, the large dimensionality of some models prevents real-time control calculations, especially on small computers. Thus, the use of simplified models is attractive because of storage and speed limitations in these computers.

Numerical model reduction techniques (Bosley and Lees, 1972) offer one approach of obtaining simple models from more complicated models. However, if one of the original system parameters changes, then the numerical model reduction process must be repeated. Therefore, the adaptive property via the measurable parameters of the original system is lost when subjected to the conventional model reduction process. Hence it would be desirable to develop reduced models which contain measurable parameters from the original system in some functional form. The only previous effort in developing low-order dynamic models which are analytical in some parameter has been due to Friedly (1972). He used a second-order Taylor series expansion for matching parameters but did not obtain analytical results for a third-order expansion.

In this paper, two methods are proposed for obtaining analytical models based on a third-order Taylor series expansion. The reduced model is specified to be of second order, since this model form is often used in process control studies. Two types of models are considered:

$$\overline{G}_{cs}(s) = \frac{b_0 + b_1 s}{1 + a_1 s + a_2 s^2} \tag{1}$$

$$\overline{G}_e(s) = \frac{K e^{-\tau_d s}}{1 + a_1 s + a_2 s^2} \tag{2}$$

$\overline{G}_{cs}$ is derived from the continued fraction expansion, while $\overline{G}_e$ is obtainable by a four-parameter matching technique. Both model forms allow for underdamped or overdamped responses.

THE CONTINUED FRACTION EXPANSION

The continued fraction expansion, which has its origin in network analysis, can yield excellent reduced models (Chen and Shieh, 1968). The continued fraction expansion operates on a general transfer function

$$G(s) = \frac{A_{21} + A_{22}s + A_{23}s^2 + \ldots + A_{2n}s^{n-1}}{A_{11} + A_{12}s + A_{13}s^2 + \ldots A_{1,n+1}s^n} \tag{3}$$

By performing long division on the fraction in the denominator, and then repeating this operation on the resulting fraction, etc., the following fraction, corresponding to a second-order transfer function, results:

$$G(s) = \cfrac{1}{h_1 + \cfrac{s}{h_2 + \cfrac{s}{h_3 + \cfrac{s}{h_4 + \ldots}}}} \tag{4}$$

where

$$h_1 = \frac{A_{11}}{A_{21}} \tag{5}$$

$$h_2 = \frac{A_{21}}{A_{12} - h_1 A_{22}} \tag{6}$$

$$h_3 = \frac{A_{12} - h_1 A_{22}}{A_{22} - h_2(A_{13} - h_1 A_{23})} \tag{7}$$

$$h_4 = \frac{A_{22} - h_2(A_{13} - h_1 A_{23})}{A_{13} - h_1 A_{23} - h_3[A_{23} - h_2(A_{14} - h_1 A_{24})]} \tag{8}$$

Note that h_1 through h_4 are developed sequentially from the coefficients of the original transfer function and do not require solution of simultaneous equations. This is a very important property of the continued fraction expansion, since unspecified parameters can be carried analytically through the development. Note also that h_4 utilizes both A_{14} and A_{24}; thus, the technique includes third-order terms in its expansion.

A second-order reduced transfer function can be developed from $h_1 - h_4$ by simple manipulation of the denominator of Equation (4):

$$\overline{G}(s) = \frac{(h_2 + h_4)s + h_2 h_3 h_4}{s^2 + (h_1 h_2 + h_1 h_4 + h_3 h_4)s + h_1 h_2 h_3 h_4} \tag{9}$$

If a higher-order reduced model is required, then more coefficients (h_5, h_6, . . .) must be developed. However, these coefficients can still be computed sequentially, so higher-order analytical transfer functions are feasible to derive.

THIRD-ORDER MATCHING PROCEDURE

The transfer function in Equation (2) can be expanded in a Taylor series so that the numerator is a constant. In the sequel, $K = 1$ is assumed, and the expansion is truncated at third order:

$$\overline{G}_e = \frac{1}{1 + (a_1 + \tau_d)s + \left(a_2 + \frac{\tau_d^2}{2} + a_1\tau_d\right)s + \left(\frac{\tau_d^3}{6} + a_2\tau_d + \frac{\tau^2_d}{2}a_1\right)s^3} \tag{10}$$

Similarly, if the original system is expanded by long division to third order, then

$$G = \frac{1}{1 + q_1 s + q_2 s^2 + q_3 s^3} \tag{11}$$

Then, by matching the coefficients and rearranging, we can obtain a cubic equation in τ_d alone:

$$\frac{-\tau_d^3}{6} + q_1\frac{\tau_d^2}{2} - q_2\tau_d + q_3 = 0 \tag{12}$$

a_1 and a_2 can be found from τ_d:

$$a_1 = q_1 - \tau_d \tag{13}$$

$$a_2 = q_2 + \frac{\tau_d^2}{2} - a_1\tau_d \tag{14}$$

Equation (12) can be solved analytically (CRC Handbook, 1961), although its application is more difficult than for the continued fraction expansion and, in some cases, can be impractical.

An example will be used to demonstrate the application of the two analytical methods, and numerical comparisons based on the integral square error (I.S.E.) will be performed for various model approximations.

EXAMPLE

We consider a mixing cell system with repeated roots

TABLE 1. COMPARISON OF TAYLOR SERIES EXPANSIONS AND INTEGRAL SQUARE ERRORS FOR REDUCED MODELS

Transfer function	Taylor series expansion for reduced models	I.S.E.*
$\text{original} = \dfrac{1}{(10s+1)^{10}}$	$G^{-1} = 1 + 100s + 4\,500s^2 + 120\,000s^3 + 2\,100\,000s^4 + 0(s^5)$	
$\overline{G}_{cs} = \dfrac{1 - 26.7s}{1 + 73s + 1833s^2}$	$G_{cs}{}^{-1} = 1 + 100s + 4\,500s^2 + 120\,000s^3 + 3\,200\,000s^4 + 0(s^5)$	1.0645
$\overline{G}_e = \dfrac{e^{-48.93s}}{1 + 51.07s + 804s^2}$	$G_e{}^{-1} = 1 + 100s + 4\,500s^2 + 120\,000s^3 + 2\,198\,000s^4 + 0(s^5)$	0.0590
$\overline{G}_f = \dfrac{e^{-68.4s}}{1 + 31.6s}$	$G_f{}^{-1} = 1 + 100s + 4\,500s^2 + 127\,200s^3 + 2\,597\,000s^4 + 0(s^5)$	0.4648

* I.S.E. $= \int_0^{500} [y(t) - \overline{y}(t)]^2\, dt.$

$$G(s) = \frac{1}{(as+1)^n} \tag{15}$$

and two unspecified parameters, a and n. This type of parametric model is often used to describe transient behavior in wastewater treatment, where the residence time (a) is subject to large variations.

Expanding the denominator in Equation (15) as a polynomial, one obtains for the first four terms

$$1 + nas + \frac{n(n-1)}{2} a^2s^2 + \frac{n(n-1)(n-2)}{6} a^3s^3 + \ldots\ (n > 3) \tag{16}$$

When we apply the formulas [Equations (5) to (8)] for the continued fraction expansion, the h_p are

$$h_2 = 1 \qquad h_3 = \frac{-2n}{n-1}$$
$$h_2 = \frac{1}{na} \qquad h_4 = \frac{-3}{na}\,\frac{n-1}{n+1} \tag{17}$$

Setting $n = 10$ and letting the residence time parameter a remain unspecified, one obtains

$$\overline{G}_{cs} = \frac{1 - 2.667as}{1 + 7.333as + 18.333a^2s^2} \tag{18}$$

Note that this reduced model will show an inverse response (minimum phase behavior).

Using the matching expansion method for $n = 10$, one obtains three possible roots for the time delay according to Equation (15):

$$\tau_d = 15.784a,\ 4.8929a,\ 9.3233a$$

However, roots one and three yield negative a_1 or a_2 (unstable system). Hence, the only admissible solution yields the transfer function

$$\overline{G}_e = \frac{e^{-4.893as}}{1 + 5.107as + 8.04a^2s^2} \tag{19}$$

Friedly's first-order model, obtained by matching second-order expansions of G and $\overline{G}$, is

$$\overline{G}_f = \frac{e^{-6.84as}}{1 + 3.16as} \tag{20}$$

In order to test the relative usefulness of the above analytical reduced models, a value of $a = 10$ was used for numerical comparisons. The I.S.E. of the above models are given in Table 1. It is interesting to note that $\overline{G}_e$ yields the best approximation, and that $\overline{G}_f$, arising from a second-order expansion, yields a lower I.S.E. than for $\overline{G}_{cs}$, which uses a third-order expansion. The reason for this occurrence can be seen by examining the third- and fourth-order terms in the Taylor series for these models, also shown in Table 1. Note that $\overline{G}_{cs}$ contains a very large error in the s^4 term relative to the other models. On the other hand, $\overline{G}_f$ provides a close match to both the s_3 and s^4 terms, the net result being a lower I.S.E. A more rigorous examination of the relative effects of transfer function coefficient errors on the I.S.E. has been performed by Edgar (1976).

The beneficial effect of including numerator terms in the transfer function for modeling higher-order systems should not go unrecognized. Examination of the Taylor series expansion shows that a time delay term creates higher-order terms in the denominator which match the higher-order dynamics. If a lower-order model with no time delay is postulated, no higher-order terms will occur in the expansion of the denominator. This will have deleterious results in the model approximation process.

CONCLUSIONS

The two analytical model reduction methods for single input-single output linear dynamic systems yield low-order models which are excellent approximations to the original system. The retention of parameters from the original model in the reduced model is a very attractive feature of this approach, and the mathematics involved are not too cumbersome. These methods have also been applied to systems with real, distinct eigenvalues with similar success.

NOTATION

a = mixing cell model parameter
a_i = denominator coefficient of transfer function
A_{ij} = transfer function coefficient
b_i = numerator coefficient of transfer function
e = exponential function
G = original transfer function
$\overline{G}$ = transfer function of reduced order
h_i = continued fraction ratio
k = steady state process gain

n = order of dynamic system
q_i = denominator coefficient of transfer function
s = Laplace domain variable
τ_d = time delay

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A Combined Heuristic and Evolutionary Strategy for Synthesis of Simple Separation Sequences

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This note presents a useful technique for merging two previously proposed strategies for synthesizing systems of simple separation sequences. The strategies are the use of heuristics (Lockhart, 1947; Rod and Marek, 1959; Nishimura and Hiraizumi, 1971; Thompson and King, 1972; Hendry and Hughes, 1972; Rudd, Powers, and Siirola, 1973; and King, 1971) and evolutionary methods. Two examples illustrate the apparent power of the approach over the use of the individual strategies alone.

Stephanopoulos and Westerberg (1976) outlined the view of evolutionary synthesis adopted here, that is, that four basic ideas are required: an initial flow sheet, rules to make systematic and small changes to the flow sheet creating what is termed a neighboring flow sheet, an effective strategy to apply these rules, and a means to compare the original flow sheet to any of its neighbors. At least fourteen heuristics have previously been proposed for synthesizing multicolumn separation sequences (Lockhart, 1976). In this note, we examine the use of the following set of six heuristics to aid in the first and third ideas above.

Heuristic 1: forbidden splits. In order to reduce the magnitude of the combinatorial problem, conduct a preliminary screening of separation methods based on an examination of various factors. While not rigorous, the graphical screening method of Souders (1964) is simple and convenient. It begins with an examination of the technical feasibility of ordinary distillation which, in principle, is applicable over the entire region of coexisting vapor and liquid phases. This region extends from the crystallization temperature to the convergence pressure, provided that species are thermally stable at the conditions employed. First, the column operating pressure is determined. If refrigeration is required for the overhead condenser, alternatives to ordinary distillation, such as absorption and reboiled absorption, might be considered. At the other extreme, if vacuum operation of ordinary distillation is indicated, liquid-liquid extraction with various solvents might be considered. In the wide intermediate region, ordinary distillation is generally not feasible economically when the relative volatility between key components is less than approximately 1.05. Even when this separation index is exceeded, extractive distillation and liquid-liquid extraction may be attractive alternatives, provided that relative separation indexes for these methods exceed those indicated by the curves plotted in Figure 3 of the Souders article or if an order of volatility (or other separation index) for these alternative methods is achieved that permits production of multicomponent products without blending. To develop these curves, Souders assumed a solvent concentration of 67 mole % and a liquid rate four times that used in ordinary distillation. In general, extractive distillation need not be considered when the relative volatility for ordinary distillation is greater than about two.

Heuristic 2: For each method, develop an ordered list of components according to volatility (or other separation index). Then, for each adjacent pair of components i and j, estimate their adjacent relative volatility $\alpha_{ij} = K_i/K_j > 1$. When the adjacent relative volatilities of the ordered components in the process feed vary widely, sequence the splits in the order of decreasing adjacent relative volatility. This heuristic is related to the heuristic, "separations where the relative volatility of the key components is close to unity should be performed in the absence of non-key components," as stated by King (1971).

Heuristic 3: Sequence the splits to remove components in the order of decreasing molar percentage in the process feed when that percentage varies widely but the rela-