Analysis of Stability of Food Emulsions by Eyring's Theory: Influence of Different Biopolymers

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ABSTRACT: Eyring's kinetic theory of liquids was applied to the study of flow behavior of low oil content mayonnaises at different temperatures. These food emulsions were formulated with different biopolymers as stabilizers (polysaccharides such as modified starch, gellan gum, and pectin). The analysis of the values obtained for the parameters of the Eyring equation for viscosity determined the emulsion containing only starch as a stabilizer is the most unstable to stirring. Replacement of part of the starch with gellan gum or pectin enhances the stability of the emulsion. The results for activation energy are quite similar for high shear rates, which can be explained by the evolution of the average drop size distribution. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 2653–2657, 2004

Key words: additives; polysaccharides; rheology; structure–property relations; thermal properties

INTRODUCTION

Food emulsions, both oil–water (mayonnaise, salad creams, or milk) and water–oil emulsions (margarine or butter)[1] are complex multicomponent systems that are thermodynamically unstable. A stable emulsion has no noticeable evolution in drop number, drop size distribution, or drop spatial distribution in the disperse phase. An emulsion becomes thermodynamically unstable basically due to the high interface area, which leads to the spontaneous aggregation of drops.[2] Emulsion stability can be increased by adding emulsifiers to reduce interfacial tension or hydrocolloids to increase viscosity, thereby reducing drop mobility. An important objective of emulsion technology is to optimize the formulation according to the desired characteristics of the final product.[3–5]

Mayonnaises are highly appreciated by consumers, but their high oil content is not in agreement with the present nutritional trend toward low calorie food products. This poses the challenge of reducing fat while retaining sensory properties equivalent to those of the standard products.[6,7] Different hydrocolloids are used to secure the desired texture and also afford emulsion stability. Normally, commercial formulations of this type of mayonnaise include modified starch, due to its special creamy texture. The combination of starch with other natural gums, such as guar, xanthan, gellan, pectin, or carboxymethyl cellulose,[8–14] can improve the quality of the product by enhancing its rheological properties.

Studying the flow behavior of food emulsions from a practical perspective implies considering a yield stress, σ_0, i.e., a finite amount of stress needed to initiate flow. This yield stress can be considered to impart stability to the emulsion in low-stress situations, such as storage or transportation. At greater shear stresses, most food emulsions show shear thinning behavior. Thus, for intermediate shear rates, the flow curve, $\sigma = f(\dot{\gamma})$, normally follows the Herschel–Bulckley model:[15]

$$\sigma = \sigma_0 + K\dot{\gamma}^n \tag{1}$$

Moreover, temperature plays an important role in the rheological behavior of emulsions. This relation is usually investigated based on empirical formulas, such as those of Voguel or Kennedy,[16–18] that can even take into consideration the non-Newtonian nature of the fluid.

On the other hand, Eyring developed an approximation based on the kinetic theory of liquids. Fluid molecules are in constant motion. However, as a consequence of the compact packing of the molecules, movement is limited to vibration within the confines of the neighboring molecules. These confines are represented by a potential energy barrier ΔG_0 for each molecule. According to Eyring, a fluid at rest undergoes continuous rearrangements whereby a molecule can escape from its confinement toward a contiguous gap.[6] As a result, the flow capacity of the system must be related to the number of possible gaps and to the corresponding free activation energy for flow, $\Delta G_0^{\ddagger}$.

If the fluid is subjected to shear stress, σ, the confinements will be distorted and the potential energy barrier will be modified. When the sense of the applied stress coincides with the fluid movement, a decrease in activation energy results:

$$\Delta G^{\stackrel{+}{}} = \Delta G_0^{+} - \Delta G(\sigma) \qquad (2)$$

Based on these considerations, the viscosity of a liquid would be expressed as:

$$\eta = A e^{(\Delta G_0^{+}/RT)} \qquad (3)$$

where A is a coefficient depending upon the free volume, V_L, of the fluid studied, expressed as $A = f(1/V_L)$.

Therefore, the Eyring theory makes it possible to estimate viscosity from other physical parameters or to account for the possible structural configuration of a fluid once its viscous behavior is known.

In this paper, different formulations of low calorie mayonnaises are studied. A fixed hydrocolloid concentration is used, though different combinations are considered, replacing part of the modified starch with pectin or gellan gum. The dependence of viscosity on temperature is analyzed using the Eyring model, i.e., relating it to the structure and stability of the emulsions.

EXPERIMENTAL

Materials

Acetylated distarch adipate (commercially C*Tex 06214) was acquired from the manufacturer (Cerestar, Barcelona, Spain). High methoxy (HM) pectin with a degree of esterification (DE) of 73.9% was provided by Tranadit (Murcia, Spain), and deacylated gellan gum (Kelcogel F) was obtained from Vedeqsa (Barcelona, Spain). Pasteurized liquid salted egg yolk, sunflower oil, and wine vinegar (equivalent acetic acid concentration: 10%) were kindly supplied by Hijos de Ybarra (Seville, Spain). Commercial salt and sugar, preservative (potassium sorbate), and deionized water were also used.

Emulsion manufacture

Emulsion formulation was adapted from the commercial composition of low oil content mayonnaise containing 4 wt % of modified starch (MS) as stabilizer and a 34 wt % of vegetable oil. The total content of stabilizer was maintained at 4 wt %, a MS fraction being partially replaced by HM pectin and gellan gum. Table I indicates the hydrocolloid content in the different formulations tested, together with the nota-

TABLE I
Hydrocolloid Combinations Considered in the Different Formulations Tested and the Notation Used in Text

Emulsions notation	Hydrocolloid content (wt)
Starch	4% MS
Pectin	3.5% MS + 0.5% pectin
0.1% Gellan	3.9% MS + 0.1% gellan gum
0.3% Gellan	3.7% MS + 0.3% gellan gum
0.5% Gellan	3.5% MS + 0.5% gellan gum

MS, modified starch.

tion used in the text below to refer to each of the emulsions.

The final manufacture method chosen consisted of two steps: the first dealt with the hydrocolloid gel formation and the second with the emulsion manufacture.

In the first stage, the solid ingredients except salt were dispersed in water and heated to 85°C while stirring for 10 min to ensure homogeneous gelation of the starch. For the emulsion containing pectin, a solution of pectin was previously prepared by stirring a dispersion of pectin in hot water. For the emulsions containing gellan gum the salt was added after the starch gel was formed to yield gellan gum gelation while cooling.

Finally, the rest of the liquid ingredients were added, together with the evaporation-induced water losses. The mixing equipment employed for emulsification was a colloid mill pilot plant (Fryma, Germany).

The final emulsions prepared were stored at 5°C until measurement.

Viscosity and drop size distribution measurements

The experimental values of shear stress were determined with a Bohlin V-88 viscometer, using the C14 wide-gap sensor (14 and 25 mm for the inner and outer cylinders, respectively). Seven up and down curves were performed for each sample (about 500 s each loop). Considering the corresponding non-Newtonian correction, the interval of shear rate used was $[7–450]s^{-1}$, with 26 points in logarithmic distribution (10 s each).

The measurements were carried out at five different temperatures between 8.5 and 26°C, regulated by a Hetoterm thermostat and a Select refrigerator. The samples were kept at the corresponding temperature for 24 h before measurement.

The drop size was determined with a Master Sizer analyzer from Halvern Instruments, which is able to discriminate drop sizes in the interval 0.5 to 180 μm, using deionized water as the dispersant medium.

The average diameter used to describe the results of the drop size distribution is the Sauter diameter $D(3,2)$ defined as:
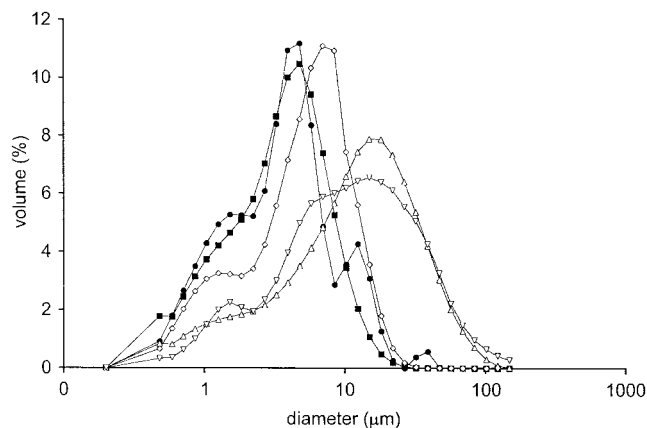
Figure 1 Particle size distribution for the different emulsions studied: (●) starch, (■) pectin, (◇) 0.1% gellan gum, (△) 0.3% gellan gum, (▽) 0.5% gellan gum.

$$D(3,2) = \frac{\Sigma d^3}{\Sigma d^2} \qquad (4)$$

Figure 1 shows the resulting drop size distribution.

RESULTS AND DISCUSSION

All the emulsions studied show shear thinning behavior. As a consequence of the experimental conditions, the curves fit very well to the Herschel-Buckley eq. (1), with a regression coefficient, r^2, of better than 0.990. Both yield stress and power law index are almost independent of temperature in any of the different formulations considered. Figure 2 shows, as an example, the flow curves obtained for the starch emulsion.

Based on the Herchley–Buckley model, the apparent viscosity as a function of shear rate, $\dot{\gamma}$, can be obtained using the following relation:
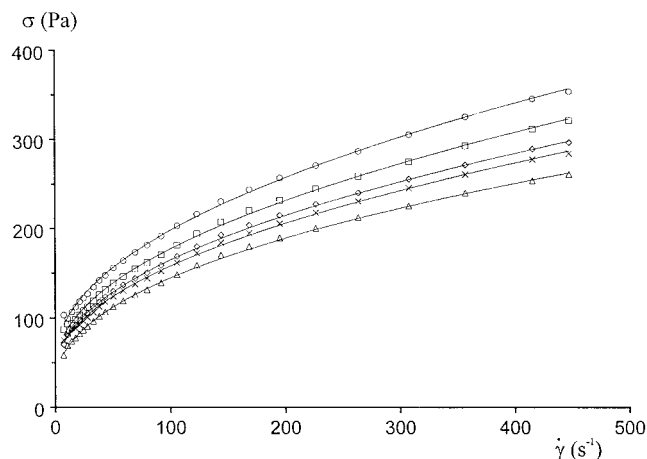

Figure 2 Flow curves for the starch emulsion at the following temperatures: (○) 8.5°C, (□) 12°C, (◇) 18°C, (×) 22°C, (△) 26°C.
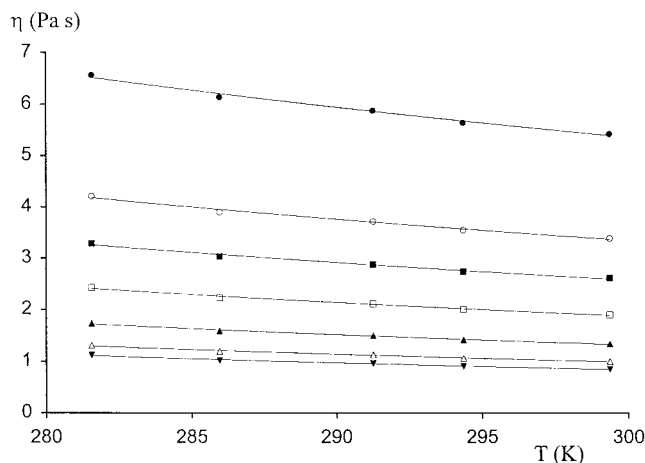

Figure 3 Viscosity as a function of temperature for the pectin emulsion at the following shear rates: (●) 20 s^{-1}, (○) 40 s^{-1}, (■) 69 s^{-1}, (□) 100 s^{-1}, (▲) 180 s^{-1}, (△) 300 s^{-1}, (▼) 400 s^{-1}.

$$\eta = \frac{\sigma}{\dot{\gamma}} = \frac{\sigma_0}{\dot{\gamma}} + K\dot{\gamma}^{n-1} \qquad (5)$$

The shear thinning behavior can be interpreted as an increase in free volume and a decrease in the total surface of the disperse phase as a result of stirring.

The temperature dependence of apparent viscosity is shown in Figure 3 for the pectin emulsion. The regression coefficient, r^2, was better than 0.990 when fitting the data to the Eyring eq. (3). The values of the parameter A and activation energy $\Delta G_0^{\ddagger}$ are analyzed in turn.

Figure 4 shows the shear rate dependence of the parameter A for all emulsions. The lowest values of A correspond to the emulsion containing only starch as
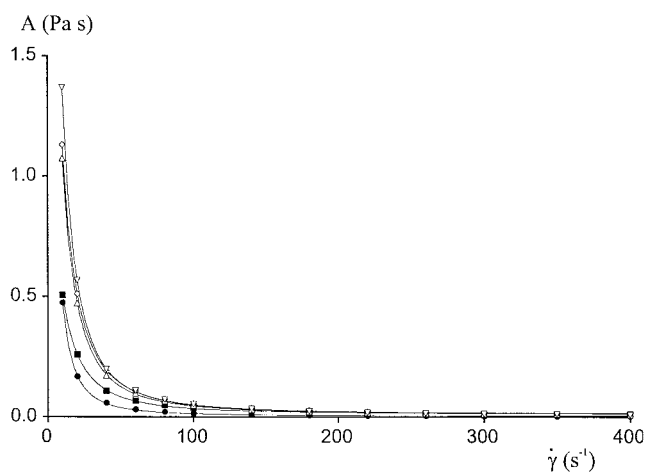

Figure 4 Coefficient A of the Eyring equation versus shear rate for the different emulsions studied: (●) starch, (■) pectin, (◇) 0.1% gellan gum, (△) 0.3% gellan gum, (▽) 0.5% gellan gum.

TABLE II
Maximum and Minimum Values of the Coefficient A of the Eyring Equation Fitted for the Different Emulsions Using eq. (6)

	A_{max} ($\dot{\gamma} = 0$) (Pa s)	A_{min} ($\dot{\gamma} = \infty$) (Pa s)	$\Phi = A_{max}/A_{min}$
Starch	4.4 ± 0.6	0.0053 ± 0.0008	800 ± 200
Pectin	1.43 ± 0.15	0.0135 ± 0.0011	110 ± 20
0.1% Gellan	4.4 ± 0.3	0.0140 ± 0.0014	310 ± 50
0.3% Gellan	4.5 ± 0.3	0.0127 ± 0.0013	360 ± 60
0.5% Gellan	7.0 ± 0.4	0.0122 ± 0.0013	570 ± 90

thickener. The results for the emulsions containing gellan gum are similar for different gum concentrations, A apparently being independent of gellan concentration. The values for the pectin emulsion are intermediate.

Continuous lines in the figure are the results of fitting the coefficient A to the following equation:

$$A = A_0 + \frac{a}{(b + \dot{\gamma})^2} \qquad (6)$$

where A_0, a, and b are constants. This equation has the adequate limit behavior for very low and very high shear rates $\dot{\gamma}$. When the shear rate $\dot{\gamma}$ approaches zero, A reaches its maximum value, $A_{max} = A_0 + a/b^2$, which means that the free volume, V_L, is a minimum. This corresponds to the unstirred emulsion formed by a homogeneous dispersion of very small drops. By stirring, the measured drop size increases through the collapse of small drops on bigger drops, as can be detected not only by measurement but also visually by oil spots on the surface. The free volume therefore increases, and A reaches a minimum A_{min} as $\dot{\gamma} \to \infty$. Table II shows the corresponding values of A_{min} and A_{max} for the fit to the model of eq. (6). The correlation coefficient is better than 0.998.

The least free volume corresponds to the 0.5% gellan emulsion and the greatest corresponds to the pectin emulsion. However, the analysis of measured drop size shows the average drop size for the former emulsion to be about 5.50 versus 2.22 μm for the latter. The free volume of the 0.5% gellan emulsion is about five-fold the free volume of the pectin emulsion. A possible interpretation would be that pectin can modify interfacial tension and the interaction between drops, leading to groups of individual drops that together form an apparent greater size drop, resulting in more free volume (lower A_{max}).

On the other hand, the minimum values of A are all similar and very small, which indicates similar free volumes for all the emulsions at high shear rates. This can be interpreted as the apparent oil drop size is the same in all emulsions under conditions of fast stirring

and is much larger than that corresponding to the unstirred emulsions.

The ratio $\Phi = A_{max}/A_{min}$ is a valuable index for evaluating the stability of an emulsion. High ratios are shown by less stable emulsions. Results in Table I indicate that the least stable emulsion is that containing only starch, while the most stable system is that containing pectin in its formulation. Therefore, substituting part of the starch by gellan gum, and especially pectin, enhances stability of flow oil content food emulsions when subjected to stirring.

The measured dependence of activation energy ΔG_0^+ on shear rate, $\dot{\gamma}$, given by eq. (3), is shown in Figure 5. On comparing the five emulsions, it can be seen that, for very low shear rates, the activation energy is very low for all cases studied. For high shear rates, the activation energy settles to a maximum $(\Delta G_0^+)_{max}$. The Eyring theory accounts for this maximum by postulating that the drag on drops of increasing size involves also the larger "holes" and, therefore, higher activation energy. However, interfacial tension does not favor the joining of droplets as the size increases. The experimental data show quite similar values of $(\Delta G_0^+)_{max}$, indicating a similar average size of droplets at high shear rates, regardless of the emulsion studied, in accordance with the results for parameter A. Only the pectin emulsion shows a $(\Delta G_0^+)_{max}$ value about 20% less than the starch emulsion.

The measured dependence of activation energy, ΔG_0^+, on shear rate, $\dot{\gamma}$, can be accurately reproduced by

$$\Delta G_0^+ = (\Delta G_0^+)_{max}(1 - e^{(-P\dot{\gamma}^m)}) \qquad (7)$$

for $m = 1/3$, with correlation coefficients, r^2, better than 0.998. Table III shows the fitted values of P and $(\Delta G_0^+)_{max}$ of eq. (7)
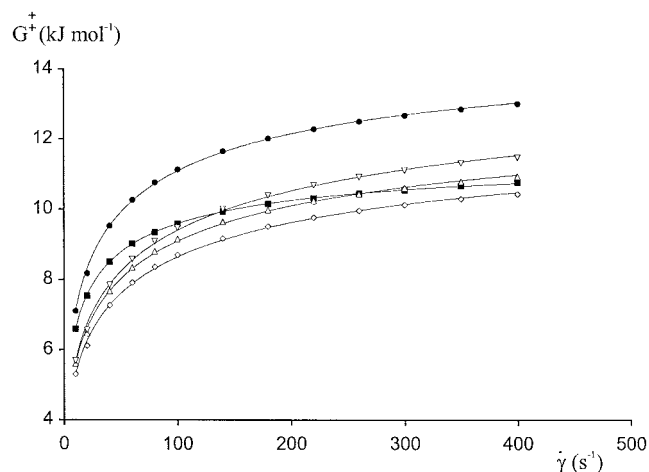

Figure 5 Activation energy versus shear rate for the different emulsions studied: (●) starch, (■) pectin, (◇) 0.1% gellan gum, (△) 0.3% gellan gum, (▽) 0.5% gellan gum.

TABLE III
Activation Energy Associated with Parameters P and $(\Delta G_0^+)_{max}$ of eq. (7) Obtained from the Measured Emulsions ($r^2 > 0.998$)

	$(\Delta G_0^+)_{max}$ (kJ mol^{-1})	P (s^m)
Starch	14.40 ± 0.06	0.315 ± 0.003
Pectin	11.29 ± 0.01	0.408 ± 0.001
0.1% Gellan	12.18 ± 0.09	0.265 ± 0.004
0.3% Gellan	12.65 ± 0.08	0.272 ± 0.004
0.5% Gellan	13.68 ± 0.12	0.249 ± 0.005

The parameter P quantifies the dependence of activation energy on shear rate. High values of this parameter, as in the case of the pectin emulsion, indicate less dependence on shear rate, whereas the gellan gum emulsions are more sensitive to shear rate but in a manner independent of the gellan concentration involved.

In a previous work,[14] we studied macromolecular dispersions of xanthan gum. Some of the conclusions drawn in that study are applicable to the present emulsions, though in reverse order relative to shear rate. For the dispersions, the molecular conglomerates existing at low shear rates develop to smaller conglomerates for higher shear rates, which corresponds to lower activation energy. On the other hand, in the case of emulsions, the small droplets existing at low shear rates become bigger when stirring increases, which means higher activation energy this time.

This opposite behavior is easily seen when comparing eq. (7) proposed here for the emulsions with the equation used for the dispersions,[14] where the parameter m was likewise 1/3:

$$\Delta G_0^+ = (\Delta G_0^+)_{max} e^{(-K_2 \dot{\gamma}^m)} \tag{8}$$

The Eyring kinetic theory for liquids considers the activation energy of eq. (3) as the energy needed for a molecule to overcome the potential barrier in moving to a nearby "hole." The theory assumes a homogeneous liquid of identical nondeformable molecules of very small size compared with our droplets.

The situation with emulsions is more complex: the droplets in this case are deformable and are polydispersed in a gel phase, while hydrocolloids in turn thicken the viscosity of the continuous phase and restrict drop mobility. The polymer molecules induce repulsive forces on near droplets and a mechanical barrier to coalescence. The rheological properties of emulsions will depend on structural parameters, such drop size and polydispersion, the hydrocolloid and its concentration, etc.

Thus, the activation energy of the Eyring theory should now include other energy terms, as droplet drag work, surface energy, droplet deformation energy, work done by repulsive forces based on adsorbed hydrocolloid molecules, and so on. These new terms account for the deviations of the original Eyring theory for simple liquids with respect to the case of emulsions.

Nevertheless, a simple model such as that afforded by the Eyring theory can be very valuable for interpreting the flow properties of emulsions. We have shown that this simple theory can be applied to complex systems, such as multicomponent formulations, to derive rules governing the stability of emulsions in relation to stirring. In our case, it can help us select the best thickeners and the most stable emulsion formulation when the fat content is decreased to produce low calorie mayonnaise.

References

1. Rahalkar, R. R. In Viscoelastic Properties of Foods. Rao, M. A.; Steffe, J. F., Eds.; Elsevier Applied Science: London, 1992; Chap 12.
2. Ferguson, J.; Kemblowski, Z. Applied Fluid Rheology. Elsevier Applied Science: London, 1991.
3. Chanamai, R.; McClements, D. J Colloids Surf A 2000, 172, 79.
4. Wendin, K.; Aaby, K.; Edris, A.; Ellekjaer, M. R.; Albin, R.; Bergenstahl, B.; Johansson, L.; Willers, E. P.; Solheim, R. Food Hydrocolloids 1997, 11, 87.
5. Moros, J. E.; Franco, J. M.; Gallegos, C. Int J Food Sci Technol 2002, 37, 297.
6. Peressini, D.; Sensidoni, A.; de Cindio, B. J Food Eng 1998, 35, 409.
7. Wendin, K.; Hall, G.; Lebensm-Wiss Technol 2001, 34, 222.
8. Cabeza, C.; Muñoz, J; Alfaro, M. C.; Flores, V. In Progress in Rheology: Theory and Applications; Martinez Boza, F. J.; Guerrero, A.; Partal, P.; Franco, J. M.; Muñoz, J., Eds.; GER: Sevilla, 2002; pp. 477–480.
9. Kulicke, W. M.; Eidam, D.; Kath, F.; Kix, M. Kull, A. H. Starch 1996, 48, 105.
10. Dickinson, E. In Food Polysaccharides and Their Applications; Stephen, A. M., Ed.; Marcel Dekker: New York, 1995.
11. Takigawa, T.; Nakajima, K.; Masuda, T. Prog Colloid Polym Sci 1999, 114, 62.
12. Jampen, S.; Britt, I. J.; Tung, M. A. Food Res Int 2000, 33, 579.
13. Fernández, M. A.; Alfaro, M. C. Muñoz, J. In Progress in Rheology: Theory and Applications; Martinez Boza, F. J.; Guerrero, A.; Partal, P.; Franco, J. M.; Muñoz, J., Eds.; GER: Sevilla, 2002; pp. 485–488.
14. Kawakatsu, T.; Trägårdh, G.; Trägårdh, C. J Food Eng 2001, 50, 247.
15. Darby, R. Emulsions and Emulsion Technology; Marcel Decker: New York, 1984; Chap. 2.
16. Dolz, M.; Hernández, M. J.; Delegido, J. J Appl Polym Sci 2002, 83, 332.
17. Bird, R. B.; Stewart, W. E.; Logthfoot, E. N. Transport Phenomena; Wiley: New York, 1960; Chap. 1.
18. van Wazer, J. R.; Lyons, J. W.; Kim, K. Y.; Colwell, R. E. Viscosity and Flow Measurement: A Laboratory Handbook of Rheology; Interscience Publishers: New York, 1963; Chap. 1.