TIME-DEPENDENT MODELS OF GRAIN-FORMING STELLAR ATMOSPHERES

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ABSTRACT

The atmospheres of many stars are variable to such a degree that they are not adequately represented by either static or steady-state models. In this study, a computer programme capable of calculating completely time-dependent model atmospheres of variable stars was developed. Specifically, the programme was developed to model the expanding atmospheres of cool, carbon-rich stars. The driving force for the expansion was radiation pressure acting on graphite grains which were assumed to form in the outer layers of the star. The details of the condensation and growth of the graphite grains as well as the resultant interactions between (a) the grains and the stellar radiation field and (b) the grains and the ambient gas were included in the calculations.

The models were calculated by coupling a model atmosphere programme to the hydrodynamical equations needed to describe the flows of the gas and the grains, and to the equations which govern the nucleation and growth of the grains. The atmospheres were assumed to be spherically symmetrical and to have a grey opacity. In addition, the thermal time scale was assumed to be negligible compared to the dynamical time scale. The grains were assumed to be spheres of graphite and to form in accordance with the Lothe-Pound nucleation theory.

The stellar parameters adopted for the models were $M = 1.5 M_{\odot}$, $L = 1.94 \times 10^4 L_{\odot}$, $C/H = 1.22 \times 10^{-3}$ and $C/O = 1.76$. The surface-free-energy adopted for the grains was 1000 ergs/cm^2 . Two time-dependent models were calculated. Model 1 had

$T^* = 2500$ K and was followed for an elapsed time of 27.3×10^7 sec. For Model 2, $T^* = 2400$ K and the elapsed time was 56.3×10^7 sec. The structure of both models was such that carbon vapour was found to be highly supersaturated in the outer layers of the atmospheres and extensive grain condensation occurred. The radiation pressure on these grains was sufficient to generate mass flows in both models. The calculated mass loss rate for Model 1 was $6.2 \times 10^{-9} M_{\odot}/\text{yr}$, and for Model 2, $7.4 \times 10^{-8} M_{\odot}/\text{yr}$. In Model 1, the mass flow approached a steady-state but in Model 2, a small amplitude pulsation was superimposed upon the outward flow. Initially, this pulsation was very irregular but after an elapsed time of 27×10^7 sec, the model had relaxed into a steady pulsation mode with a period of 6.48×10^7 sec and a velocity amplitude at the surface of 0.8 km/sec. This mode was followed for four periods during which the amplitude of the pulses remained constant. The driving force for this pulsation appears to be an opacity controlled feedback mechanism which operates between the grain-forming region of the model and the hydrogen dissociation zone. It was found that in Model 1, the opacity of the grains was too small for this mechanism to produce pulsations.

In both models, grain nucleation was negligible at supersaturation levels less than 5. As a result, the grain-forming region was restricted to layers for which $r > 1.82R^*$ in Model 1, and $r > 1.58R^*$ in Model 2. In both cases, the low atmospheric densities in the grain-forming regions severely limited the growth of the grains following their formation so that the grains remained very small ($a \approx 5.5 \times 10^{-8}$ cm) and, even

at the surface of the models, only about 75% of the free carbon vapour was in the form of grains. The optical depth of the grains at $\lambda = 0.7\mu$ was 5.0×10^{-3} in Model 1, and 1.0×10^{-1} in Model 2. The pulsation in Model 2 produced a variation in the optical depth of the grains of 1.8×10^{-2} .

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Chapter I

INTRODUCTION

In 1935, Adams and MacCormack noted that the cores of several strong resonance lines in four M stars were blue-shifted by about 5 km/sec. On the basis of this evidence, they inferred that each star was gradually losing mass from an expanding circumstellar shell. Since these first observations, evidence has accumulated that suggests that all red giant stars¹ later than M0 are losing mass to the interstellar medium at a rate greater than $10^{-5} M_{\odot}/\text{yr}$ (Reimers, 1975; Hagen, 1978). However, while mass loss rates are frequently quoted for red giants, it is important to keep in mind that these rates are rather poorly determined from the observational data. For example, the mass loss rate determined for Betelgeuse by five different investigators ranges from $3.5 \times 10^{-5} M_{\odot}/\text{yr}$ to $1.7 \times 10^{-4} M_{\odot}/\text{yr}$ (Bernat, 1977). What is very clear from the observational data is that the flow rates are quite high, and that the atmospheres of such stars cannot be adequately represented by static models.

One basic question underlying the study of mass loss from red giants concerns the cause of the atmospheric flow. Many mechanisms have been suggested (Cassinelli, 1979). Among these, is the suggestion that mass loss in very late red giants is the

¹ The term, red giant, unless otherwise qualified, will be understood to include supergiants as well as giants throughout this thesis and to imply $T_e < 4000\text{K}$.

result of the formation of atmospheric grains. According to this hypothesis, radiation pressure will expel the grains and, if the ambient gas is sufficiently coupled to the grains, it will be driven outward as well. When Weymann analyzed this mechanism in 1962, he rejected it on the basis that there would be insufficient coupling between the grains and the gas to expel the atmosphere. In the same year, Hoyle and Wickramasinghe (1962) demonstrated that grains of graphite could precipitate in the atmospheres of cool, carbon-rich stars, and that such grains may be the source of much of the interstellar reddening material. However, Weymann's analysis appeared to rule out radiation pressure on grains as being effective in causing mass loss from these stars until Gilman (1972) noted that Weymann had not considered the effects of collisions between gas molecules. It is through these collisions, that the momentum that is transferred from the radiation field to the grains is diffused through the gas. Gilman demonstrated that the grain-gas momentum coupling is sufficiently large under conditions relevant to red giants that radiation pressure on the grains can cause appreciable mass loss rates.

Although it has now been adequately demonstrated that radiation driven mass flows are kinematically possible (Wickramasinghe, et al, 1966), the controversy as to whether or not such flows are actually established in red giants remains unresolved (see, for example, Fusi-Pecchi and Renzini, 1976, Hagen, 1978, Cassinelli, 1979). The strongest argument in support of this driving mechanism is the observation of extensive, expanding dust shells surrounding all cool giants

(Merrill, 1977). What remains uncertain, is (a) can the dust grains really form in the atmosphere of a red giant? and (b) assuming the conditions for grain formation do prevail, do the grains cause the mass flow or are they merely a consequence of it?

(a) Statement of the Problem

The question of the viability of the radiation pressure driving force has remained unresolved largely because of the lack of appropriate, evaluative models. Without such models, it has been impossible to be sure whether or not this mechanism can generate a mass flow of the type actually observed. In the last decade or so, enormous improvements in the modelling of static atmospheres of red giants have been realized. Attempts to produce dynamic models have focussed largely on the kinematics of the problem and have assumed either steady or regularly pulsating flows to simplify the computational difficulties of the models. Such models are inherently incapable of representing the irregular flows which are characteristic of most red giants. For a proper representation of the atmospheres of red giants, a completely time-dependent approach is required. Consequently, the essential problem of this thesis was the development of a computer programme capable of generating time-dependent model atmospheres. This programme was then used to test the hypothesis that radiation pressure on grains is a viable mass loss mechanism in the atmospheres of red giants. Specifically, the programme was designed to model the expanding atmospheres of

cool, carbon-rich, grain-forming red giants by integrating the equations of hydrodynamics and those describing the nucleation and growth of grains with the equations used to construct a model atmosphere.

The dynamical properties of grain-forming atmospheres are numerous and complex. It was predicted that graphite grains would nucleate, grow and/or evaporate; radiation pressure acting on the grains would drive them and, perhaps, a portion of the atmospheric gas outwards; structural changes in the atmosphere would occur; and the formation and growth of the grains might be significantly altered as a consequence of these structural changes. Whether or not these interactions would produce a steady flow was not obvious. Therefore, a second and necessary purpose of the study was to see if the time-dependent models would relax to steady-state models similar to those calculated by Lucy (1976) for cool carbon stars.

The model development required an extensive analysis of existing modelling procedures, of theories pertaining to possible mass loss mechanisms, and of empirical data related to mass loss from red giants. This data is summarized in Chapter II. The model, and its underlying assumptions and limitations, are described in Chapter III. The solution algorithm is presented in Chapter IV, followed by the results of the study in Chapter V. The discussion of the results and the conclusions of the study are presented in Chapter VI. In addition, the thesis contains two appendices. The results of several numerical tests of the programme are summarized in Appendix A, and details of the homogeneous nucleation theory are presented in Appendix B.

Chapter II

BACKGROUND TO THE PROBLEM

The basic equations and physics necessary to construct model atmospheres have been known for many years but progress in the field has been slow because of the lack of knowledge of fundamental atomic quantities, and the mathematical difficulties inherent in the problem (Auer, 1971). For modelling purposes, stellar atmospheres are generally assumed to be static, plane-parallel and horizontally homogeneous, to contain only continuum opacities, and to satisfy the constraints of radiative and local thermodynamic equilibrium. The relaxation of any of these constraints greatly increases the time required to compute a model atmosphere. Ideally, none of these constraints should be used to construct models of M- and N-type stars for none of these assumptions is truly valid for red giants with $T_e < 3000$ K (Tsuji, 1978). Although some progress has been achieved in treating departures from local thermodynamic equilibrium, plane-parallel geometry and hydrostatic equilibrium, research related to model atmospheres of very cool stars has been primarily focussed upon developing techniques to include the spectral line-blanketing effects of atomic and molecular line opacities. This effort has yielded reasonably accurate line-blanketed models of all but the coolest late-type stars (Carbon, 1979). The results of this research will be briefly reviewed at the beginning of this chapter. In the second section of this chapter, the observational data on mass loss from red giants

will be summarized. This chapter will conclude with a short discussion of theories and models of suggested mass loss mechanisms.

(a) Model Atmospheres

The opacity of many overlapping atomic and molecular absorption lines is known to affect both the emergent spectrum of the star and the structure of the atmosphere itself. A concise review of the effects of various molecules on the structure of stellar atmospheres has recently been published by Gustafsson and Olander (1979). In a more extensive review, Carbon (1979) discusses the physics underlying these complicated line-blanketing effects as well as their structural consequences. In that review, Carbon states that the principal structural effects of line-blanketing are a) a heating of the continuum forming levels ($\tau > 0.1$) of the atmosphere, a phenomenon referred to as "backwarming", and b) a cooling or heating of the surface layers ($\tau < 10^{-3}$), as compared to the temperatures computed for these same levels in an unblanketed atmosphere with the same effective temperature. In both of these reviews, it is stressed that the structural effects of molecular line-blanketing are strongly correlated with atmospheric composition, micro-turbulence and atmospheric velocity gradients, and can affect the temperatures of the models by several hundred degrees.

Among the important conclusions that have been drawn from the line-blanketed models of red giants are the following:

- 1) The line blanketing of CO cools the surface temperature

of all red giants (Johnson, 1973; Gustafsson et al, 1975). This cooling effect is very temperature dependent. It is small in models with $T_e < 4500$ K, and negligible in models with $T_e < 2400$ K and $T_e > 5500$ K (Johnson, 1973).

2) The CO cooling in models with $T_e < 4500$ K is insensitive to large changes in the overall metal abundance of the models suggesting that the cooling was "saturated" (Gustafsson, et al, 1975).

3) The line-blanketing of CO produces only a small backwarming in the models (Querci and Querci, 1975).

4) The line-blanketing of all but the reddest bands of H_2O heats the surface layers of oxygen-rich stars (Carbon, 1979).

5) C_2 contributes little to the surface cooling of models (Querci and Querci, 1975).

6) The opacity of TiO leads to a global heating of the models but this effect is strongly moderated by the presence of other molecules especially CO, H_2O and CN (Krupp et al, 1978).

7) The surface warming of TiO reaches a minimum value in models with $T_e = 3000$ K whereas its backwarming effect decreases monotonically with decreasing effective temperature (Krupp et al, 1978).

8) TiO and H_2O are less effective in backwarming the continuum layers of the models than are CN and C_2 (Tsuji, 1978, Querci and Querci, 1975).

9) The backwarming effect of CN increases steadily with the metal abundance of the models (Gustafsson et al, 1975).

The structure of red giants is known to be dependent upon the C^{12}/C^{13} ratio. Carbon (1974) found that increasing the

C^{13} abundance from $C^{12}/C^{13} = 90$ to $C^{12}/C^{13} = 10$ decreased the temperature of both the continuum layers and the surface layers. It has also been demonstrated that the structure of carbon star atmospheres is moderately dependent upon the value of the micro-turbulence used to calculate the models (Gustafsson, et al., 1975). In contrast, the line blanketing effects in the atmospheres of other late-type stars are only slightly affected by variations in the micro-turbulence parameter (Tsuji, 1978; Carbon, 1974).

The principal effect of including the extension of the atmosphere in the models is to lower the temperature and gas pressure near the surface (Watanabe and Kodaira, 1978). These investigators also found that the extension of the atmosphere enhanced the spectra of molecules such as TiO and H_2O which are formed preferentially near the surface of the models, while it suppressed the spectra of molecules such as CO which are formed deeper in the atmosphere. Such effects can clearly affect the backwarming and surface temperature modifications of the various molecular species formed in the spectra of late-type stars. Although not included in their study, CN is also formed deeper in the atmosphere than TiO and H_2O so it seems likely that the structural effects of this molecule are likewise overestimated by plane parallel models.

(b) Observations of Mass Loss from Red Giants

As Mullan (1978) notes, "the detection of a circumstellar shell indicates unambiguously that the red giant is losing mass". The existence of circumstellar shells is

indicated by the analysis of optical, infrared and radio spectra of red giants. The results of such analyses are summarized in this section; more complete reviews of these topics are presented by Reimers (1975, 1978), Merrill (1978) and Moran (1976).

Most of the early observations of mass loss in red giants were restricted to the H and K lines of Ca II which are always the strongest circumstellar lines in M giants (Deutsch, 1960). However, mass loss is also manifested in the asymmetries or weak P-Cygni-type profiles of many strong, low excitation lines of neutral metals such as those of Na I at $\lambda\lambda$ 5890 and 5896, and Al I at $\lambda\lambda$ 3944 and 3961; in the lines of singly ionized metals such as that of Sr II at λ 4077; and, occasionally, in H $_{\infty}$ (Boesgaard and Hagen, 1979). Such profiles are interpreted as arising from the superposition of the blue-shifted, circumstellar line on the (presumed) unshifted photospheric line.

Numerous infrared molecular absorption bands as well as a general infrared excess arising from circumstellar shells are detected in the spectra of both M and N giants. The infrared excess is seen in all M giants more luminous than a limit defined on the HR diagram by M6 III, M5 II and M1 Iab (Reimers, 1975), and is well correlated with high luminosities and low surface temperatures (Cohen and Gaustad, 1973). The emission features at 9.7μ and 18μ in these stars are attributed to the optically thin emission from small silicate particles (Woolf and Ney, 1969). Infrared emission is detected in N stars at 11.5μ and is attributed to grains of SiC (Gilra, 1973; Treffers and

Cohen, 1974). However, the primary constituent of the dust in carbon-rich circumstellar envelopes is relatively featureless, and is detected only as a general veiling of the photospheric lines (Forrest et al., 1975), and a pronounced deficiency in the blue and ultraviolet spectral region (Mendoza and Johnson, 1965). This constituent is generally identified as graphite grains, the opacity of which varies as λ^{-2} (Gilman, 1974). The infrared data on circumstellar dust suggests that the dust is concentrated beyond the main acceleration zone of the flow (Reimers, 1975) but the distribution is difficult to determine accurately because of the lack of sharp spectral features associated with the dust (Cassinelli, 1979).

The evidence for mass flows in red giants has been enhanced in the last few years by the observation of both maser and non-maser emission from the circumstellar shells (Wilson and Barrett, 1972; Morris and Alcock, 1972). The dusty circumstellar envelopes are ideal environments for the generation of the infrared photons necessary to excite the upper vibrational levels of various molecular species. The most thoroughly studied lines are the maser lines of OH and H₂O (Wilson and Barrett, 1972), and of SiO (Morris et al., 1979; Buhl et al., 1975). Non-maser emission from SiO has been detected in the expanding envelopes of 15 red giants, one of which is carbon rich (Morris et al., 1979), and from CO in a sample of cool, oxygen rich (Lo and Bechis, 1977) and carbon rich (Zukerman et al., 1977) stars. One suspected case of weak maser CO emission has been reported (Morris, 1980).

Mass loss rates have been derived from observations

made in all three spectral regions. Hagen (1978), Sanner (1976), Boesgaard and Hagen (1979), and Bernat (1977) have calculated the mass loss rates for a total of seventy different M stars using optical data. They calculate mass loss rates ranging from a maximum of $3.8 \times 10^{-6} M_{\odot}/\text{yr}$ for the M1-M2 Iab star, 6 BU Gem (Sanner, 1976) to a minimum of $2 \times 10^{-9} M_{\odot}/\text{yr}$ for the M2-5 II-III star, β Peg (Hagen, 1978). Gehrz and Woolf (1971, see, also, Reimers, 1975) derived mass loss rates from broadband photometric measurements at effective wavelengths of 3.5, 4.9, 8.4 and 11μ for a wide variety of M stars. Representative rates are $9 \times 10^{-8} M_{\odot}/\text{yr}$ for α Her, (M5 Ib-II), $7 \times 10^{-7} M_{\odot}/\text{yr}$ for α Ori (M2 Iab) and $7 \times 10^{-6} M_{\odot}/\text{yr}$ for BC Cyg (M3.5 Ia). The mean rate of mass loss obtained for Mira variables was $2 \times 10^{-6} M_{\odot}/\text{yr}$. A trend towards higher rates for the longer period, cooler Miras was detected. In the radio region, mass loss rates are derived from the line intensities of the non-maser lines. The intensity of such lines is proportional to $f\dot{M}$ where, for example, for CO emission, $f = [\text{CO}]/[\text{H}_2]$, and $\dot{M}$ is the rate of mass loss. An independent measure of either f or $\dot{M}$ is required to determine the other. For example, assuming solar abundances for the envelopes of 15 cool, oxygen rich stars, Morris et al., (1979) calculated mass loss rates in the range ($1.7 \times 10^{-9} M_{\odot}/\text{yr}$ to $2 \times 10^{-7} M_{\odot}/\text{yr}$) from the SiO lines. As these rates were all one to two orders of magnitude lower than the rates derived by Gehrz and Woolf (1971) from infrared data, and two to three orders of magnitude lower than the average rates Elitzer et al. (1976) require to account for OH maser emission, it was concluded that up to 99% of the Si in these envelopes has condensed into

grains.

The large differences in the mass loss rates that are given for the four stars that are common to all the optical studies (Hagen, 1978) reflect the seriousness of the errors inherent in all of these calculations. Probably, the rates quoted by Hagen, and Boesgaard and Hagen, which are based upon both optical and infrared data are the most accurately determined. They are also, consistently the lowest. Most mass loss rates quoted in these and other studies give values of about $10^{-7} M_{\odot}/\text{yr}$ for M supergiants, and $10^{-8} M_{\odot}/\text{yr}$ for M giants.

(c) Mass Loss Mechanisms

The observations of mass loss from red giants suggest a driving mechanism that varies slowly with the stellar parameters but which is similar in all spectral and composition sub-classes. There are, basically, two candidate driving mechanisms for red giants (Fusi-Peccì and Renzini, 1976): (1) a solar-like wind from a non-thermally heated stellar corona, and (2) radiation pressure on dust grains. In addition, several hybrid models have been suggested (see, for example, Kwok, 1975) as has the action of radiation pressure on the molecular bands (Maciel, 1976).

Stellar winds have been suggested as a mass loss mechanism in red giants for many years (see, for example, Weymann, 1962, 1963; Parker 1961; Cassinelli, 1979 and references therein). This model is based upon the postulate that energy is deposited in a thin shell at the base of the corona. The outer atmosphere expands as a result of a build-up of the

pressure gradient that ensues. The source of the deposited energy is not specified explicitly but is supposed to arise either from turbulence in high-lying convective zones, or from acoustic or mechanical waves generated in some manner in the subphotospheric layers of the star. It is this lack of specification of the coronal heating mechanism that is the major shortcoming of the theory (Mullan, 1978). However, Hearn (1975), on the basis of his "minimum flux coronal model" argues that the coronal structure is determined by the magnitude of the (unidentified) mechanical flux input.

As an aid to developing stellar wind models, Reimers (1975) searched for a correlation between mass loss rates and fundamental stellar parameters. The relationship which appeared to best fit the empirical data was (Reimers, 1977)

$$dM/dt = 1.4 \times 10^{-13} L/gR \quad (\text{II-1})$$

where L , g and R are all in solar units. Alternatively, this expression can be written as $0.5 M v_{esc}^2 = 10^{-13} L$ which, to quote Cassinelli (1979) "implies that a constant fraction of the stellar luminosity is being used to provide the necessary energy for escape of the expanding material". Reimers (1977) also derived the empirical relationship, $v_{ter} \propto v_{esc}^2$, from the available data on mass loss rates.

Mullan (1976; see also, Cassinelli, 1979) has modified Hearn's (1975) minimum flux theory to model mass loss from red giants. On the basis of this theory, Mullan predicts that an evolving star should shift rather suddenly from a coronal

structure characterized by a low mass loss rate like that of the sun, to one dominated by high mass loss. The transition should occur when the sonic point in the flow reaches far enough below the base of the corona that spicules from the relatively dense, turbulent, chromospheric gas enter the supersonic regime of the expanding gas. Observations suggest that such a transition exists (Reimers, 1977). Also, Mullan derives the mass loss relationship

$$dM/dt = 1.6 \times 10^{-9} M R^{0.5} \quad (\text{II-2})$$

which is functionally quite different from Reimers' relationship, but which also fits the observational data quite well.

Arguments for (Mullan, 1978) and against (Vaiana and Rosner, 1978) the Hearn-Mullan model have appeared in the literature. The arguments against this model are directed at some of the assumptions on which it is based. Arguments in support of the model stress that hot coronae have been detected in some late type stars, and that the stellar wind mechanism is the only viable mass loss mechanism in atmospheres that appear to be too hot to permit significant grain formation. Further, Hagen (1978), and Boesgaard and Hagen (1979) feel that mass flows originate in the chromosphere and, for early M giants at least, are best interpreted as arising from a stellar wind mechanism. Reimers (1975) reached a similar conclusion. However, Weymann (1960) and De Jager and De Loore (1971) state that while stars with $g < 100 \text{ cm/sec}^2$ may have chromospheres, they do not

have coronae so it is difficult to understand how the Mullan model could operate in late type giants and supergiants.

The idea that radiation pressure on dust grains might lead to significant rates of mass loss in red giants was revitalized by the suggestion of Hoyle and Wickramasinghe (1962) that interstellar graphite grains may originate in the atmospheres of carbon stars. Gilman (1974) demonstrated that the grains most likely to form in M giants are silicates of various compositions (eg. MgSiO_3) and metallic iron, and in N giants, graphite and silicon carbide. The abundant evidence for the presence of dust in such envelopes (Merrill, 1978) makes a plausible case for the operation of this mechanism.

The formation of atmospheric graphite grains has been studied by various groups (Donn et al., 1968; Wickramasinghe et al., 1966; Fix, 1969; Dorfeld and Hudson, 1973; Tabak et al., 1975; and Salpeter, 1974a,b). The details of the process of small grain nucleation have been closely examined by Draine (1978), Draine and Salpeter (1977) and Yamamoto and Hasegawa (1977), especially for the case of silicate grains. The whole topic of the formation and destruction of stellar and interstellar dust grains is the subject of recent reviews by Salpeter (1977) and Greenberg (1978).

In a study in which the pulsational period of an N Mira variable was simulated, Fix (1969) developed a set of growth rate equations for dust grains. His model predicted copious graphite formation during part of the cycle of a 2050 K star but the study did not account for the fact that the grains were forming in a hydrogen rich environment. In 1974, Salpeter

demonstrated that the formation of C_2H_2 and CH_4 in cool, carbon rich atmospheres reduces the abundance of carbon vapour to the point that no condensation of graphite grains can occur above a temperature of about 1700 K. He also showed that silicates cannot precepiitate in oxygen-rich atmospheres above temperatures in the order of 1200 K. These restrictions severely limit the conditions under which grain formation can be expected to occur in stellar atmospheres. In a second paper, Salpeter (1974b) developed a set of qualitative relationships by which the characteristics of the mass flow can be predicted, given the basic parameters of the model such as M , L , grain size and composition, and the relative mass fraction of condensed material. These relationships are very useful for gaining insight into a process which results from the complex interaction of many variables.

Models of radiation driven mass flows have been constructed by Kwok (1975), for M giants, and by Lucy (1976) for N stars, for a variety of representative stellar parameters. Both studies predicted that radiation pressure on grains produces significant mass loss rates. However, both of these studies were based upon assumed characteristics of the dust grains. The nucleation and growth of the grains were not explicitly included. Kwok's models were restricted to the optically thin region of the envelope. Grains of a fixed size were assumed to form at the base of the shell and grow as they moved outward. Mass loss rates of the order of $1 \times 10^{-6} M_{\odot}/\text{yr}$ were predicted provided that the grains condense at a point in the atmosphere where the gas density is relatively large. Since this

condition is not generally fulfilled in giants later than about M3, Kwok suggested that convective turbulence could reduce the pressure scale heights in the late giants to a degree sufficient for the grain mechanism to be effective. Partial destruction of grains via sputtering when the drift velocities exceeded 20 km/sec kept the gas flow velocities of these models within the observational limits.

Lucy's (1976) models of expanding, cool ($2000 \text{ K} \leq T_e \leq 2750 \text{ K}$) carbon stars incorporated a better treatment of the atmospheric gas than did Kwok's, but again, grains of a constant radius (0.01μ , in this case) were assumed. Sudden grain formation and complete precipitation of the condensable material at the sonic point were also assumed. Lucy found that the expanding atmospheres were structurally quite different from the comparable static ones - the pressure at a given temperature was lower, and the extension, greater. The mass loss rates predicted by these models ranged from about $1 \times 10^{-7} M_{\odot}/\text{yr}$ at $T_e = 2750 \text{ K}$ to about $1 \times 10^{-5} M_{\odot}/\text{yr}$ at $T_e = 2000 \text{ K}$. A comparison of the emergent spectra of these models with observational data led Lucy to conclude that the redistribution of the radiation in these models was excessive, probably as a result of an overproduction of grains, or an underestimate of the grain radius.

The formation and structure of dusty circumstellar shells by radiation driven mass flows have been modelled by Goldreich and Scoville (1976) and Jones and Merrill (1976). These models demonstrate that by adjusting the size of the grains and the mass loss rates (both input parameters for these

models), the infrared spectral characteristics of red giants can be accurately reproduced. Menietti and Fix (1978) have produced models in which the radiative and dynamic interactions of the gas and grains were treated explicitly. They calculated mass loss rates ranging from $3.8 \times 10^{-7} M_{\odot}/\text{yr}$ to $4.9 \times 10^{-7} M_{\odot}/\text{yr}$ for M giants. A radius of 0.1μ was assumed for the silicate grains.

In all of these investigations, the properties of the mass flow depended upon the properties of the gas at the sonic point. With decreasing effective temperature, the sonic point (which was also assumed to be essentially the condensation point) moves inward to regions of higher gas density resulting in greater mass loss rates in accordance with the empirical data (Merrill, 1978).

Deguchi (1980) has modelled the nucleation and growth of silicate grains in cool stellar envelopes. By using a series of fitting equations and iterative techniques, he was able to predict the terminal flow velocity, the grain density, the final grain size and the amount of condensable Mg remaining in the envelope for specified values of M , T , L and dM/dt . These models predict an upper mass limit of $1.5 M_{\odot}$ for which the radiation pressure acting on silicate grains can drive mass flows. They also indicate that the terminal velocity of the flow and the final grain size increase with the mass loss rate and decrease with luminosity.

The models of Kwok (1975), Lucy (1976), Goldreich and Scoville (1976), Jones and Merrill (1976), Menietti and Fix (1976), and Deguchi (1980) all assumed steady-state flows. However steady-state models cannot adequately represent the mass

flows from Mira and semi-regular variables; they cannot mimic the irregular fluctuations observed in many N and late M giants; they cannot reproduce the sporadic mass ejections of R Cor Bor stars; and they cannot explain apparent long term variations in mass loss rates. Moreover, even for stars such as α Ori, which have very stable circumstellar shells, the acceleration region of the flow is obviously variable, and the shells appear to consist of distinct layers (Sanner, 1976). Furthermore, Morris et al., (1979) have found that the circumstellar expansion velocity and the period of the underlying star are correlated in red giants. This correlation suggests that the mass loss process itself is linked to pulsation. No correlation has been found between the mass loss rate and the stellar type, C/O ratio, or the constitution of the grains. The analysis of such variable atmospheric phenomena requires time-dependent models.

Lucy and Solomon (1967) predicted that red giants become dynamically unstable when the mass in the ionization zone is sufficient to reduce the average ratio of the specific heats in the envelope below $4/3$. Subsequently, the possibility of mass loss from dynamically and pulsationally unstable stellar envelopes has been extensively studied (see Tuchman et al., 1978 and references cited therein). Contrary to what was initially expected, dynamic instability alone produces only steadily pulsating models accompanied by little or no mass loss rather than the rapid ejection of the whole envelop. Radiative losses at the surface effectively damp the instability. At elevated luminosities, however, the instability leads to violent oscillations and some mass loss.

Chapter III

THE TIME-DEPENDENT MODEL

Comparisons among different models of similar atmospheres are difficult to make accurately unless the approaches encompass the same general assumptions and selection of physical parameters. This problem is particularly pronounced for red giants because of their diverse and complex properties. Since the time-dependent models to be calculated in this study were to be compared to the steady-state models calculated by Lucy (1976), it was decided to base the models on Lucy's approach insofar as it was possible to do so. In particular, many of the physical parameters and model assumptions were identical in the two approaches. The assumptions and limitations of the time-dependent models will be described in this chapter. The most significant difference between the two approaches was in the dynamical treatment of the problem. Where Lucy assumed a condition of steady flow and sudden grain formation at the sonic point, the present models incorporated a complete time-dependent treatment of the atmospheric flow, of the nucleation and growth of the carbon grains, and of the resultant interaction between the grains and the gas. The mathematical description of this approach concludes this chapter.

(a) Assumptions and Limitations of the Models

For the purposes of this study, the following assumptions were utilized:

Assumption 1: Atmospheric Composition

The atmosphere was assumed to consist of carbon vapour, an inert gas (mainly hydrogen and helium), and, possibly, carbon grains. Normal solar abundances (Allen, 1973) were assumed for all elements except that the relative CNO abundances were set at $C:N:O:H = 1.22 \times 10^{-3}:8.71 \times 10^{-5}:6.94 \times 10^{-4}:1$ to give a C/O ratio of 1.76.

Assumption 2: Spherical Symmetry

The atmospheres were assumed to be spherically symmetrical and mass flows were assumed to be radial only. In calculating the gravity of the models, the radial extension of the atmosphere was allowed for but it was assumed that the mass of the atmosphere ($\approx 0.1M_{\odot}$) was negligible compared to that of the star ($M^* = 1.5M_{\odot}$), i.e., $g(r) = GM^*/r^2$.

Assumption 3: Grey Opacity

The atmospheric opacity of late type giants is strongly frequency dependent. However, the assumption that the stellar opacity was grey was adopted for this study to reduce the computation costs of developing the computer programme and

of producing the models. The opacities of both the gas and the grains were represented by their Rosseland means.

Assumption 4: Local Thermodynamic Equilibrium

It was assumed that the stellar atmospheres satisfied the condition of local thermodynamic equilibrium (LTE). The assumption of LTE is generally valid when the occupation numbers of the atomic and molecular levels are determined by collisional processes. However, in the presence of a strong radiation field and low atmospheric densities, the atomic and molecular transitions will be dominated by radiative, not collisional processes. If LTE were not assumed, it would have been necessary to obtain a self-consistent, simultaneous solution of both the radiative transfer and the statistical equilibrium equations.

Assumption 5: Convective Stability

The atmospheres were assumed to be convectively stable. This assumption was justified on the basis of the well known inefficiency of convective transport in the upper atmospheres of red giants (Auman, 1969). The conditions necessary for grain nucleation are typically found at small optical depths (i.e. well above the layers where convective mixing is likely to occur unless overshooting of the convective zone is strong). Consequently, the models were extended only to the bottom of the H_2 dissociation zone where the atmosphere was assumed to be only marginally unstable against convective motions.

Assumption 6: Radiative Equilibrium

The assumption of radiative equilibrium implies that the atmosphere is static (Mihalis, 1978) and that the total energy transport is radiative (i.e., the luminosity is constant throughout the atmosphere). In a non-static situation, the assumption of radiative equilibrium can be justified only if the thermal time scale is less than the dynamical time scale and can be set equal to zero. The thermal time scale is defined as

$$\tau_{th} = E/L \quad (III-1)$$

where E is the total energy in the atmosphere, and L is the luminosity. The dynamical time scale is

$$\tau_d = \Delta R / \langle c \rangle \quad (III-2)$$

where ΔR is the depth of the atmosphere, and $\langle c \rangle$ is an average value for the speed of sound for the atmosphere. For M- and N-type stars, τ_{th} has a value of about 5×10^6 sec, and τ_d , about 5×10^7 sec. Thus $\tau_{th} < \tau_d$ and radiative equilibrium can be assumed as a first approximation in the development of time-dependent models. Physically, the condition $\tau_{th} < \tau_d$ means that thermal changes occur more rapidly in these stars than do dynamical changes. Mathematically, the assumption of radiative equilibrium means that changes in one part of the atmosphere are instantaneously communicated to the other parts. As a specific example, changes in the surface opacity as the result of grain formation there are immediately reflected in a change of

temperature throughout all the lower layers.

Assumption 7: Graphite Grains

The carbon grains were assumed to have the same structure and properties as ordinary graphite. Specifically, the vapour pressure, the extinction coefficient, and the Lothe-Pound factor of graphite were used. In addition, the surface-free-energy of the grains was put equal to 1000 ergs/cm^2 , a value Tabak et al, (1975) have suggested for graphite grains.

Assumption 8: Spherical Grains

The graphite grains were assumed to be small, non-deformable, spherical particles uniformly dispersed throughout the gas. Wickramasinghe (1972) has suggested that graphite will form as platelets rather than spheres at low pressures. However, because of the high degree of supersaturation required for significant grain nucleation to occur, Donn et al, (1968) concluded that the grains will be nearly spherical, non-polarizing polycrystalline grains (i.e., soot-like). The relatively flat wavelength dependence of the intrinsic polarization in N stars supports this conclusion.

Assumption 9: Classical, Homogeneous Grain Nucleation

It was assumed that the grains formed essentially according to the classical nucleation theory first developed by Volmer and Webber (1926). This theory is summarized in Appendix B. The modifications that were made to the classical theory were

the inclusion of the Lothe-Pound factor, Γ , (Lothe and Pound, 1962), the Zeldovich non-equilibrium factor, Z^* , (Zeldovich, 1942), and the allowance for the nucleation from associated vapours (Katz, et al., 1966). Salpeter (1974a) and Draine (1978) have argued that ionic nucleation should be relatively unimportant for the formation of graphite grains so only homogeneous nucleation was considered.

Assumption 10: Kinetically Governed Grain Growth

The mass exchange rate between a vapour and its condensed state is governed by the slower of the two processes: (1) the kinetic rate at which the vapour molecules collide with, and adhere to the grain surface, and (2) the rate at which the vapour molecules diffuse through the gas to the vicinity of the grain. Generally, if an inert gas is present, diffusive transport governs the mass exchange rate, whereas in a pure vapour, diffusion is non-existent, and the mass exchange rate is controlled only by the kinetic flux. Although carbon vapour will form only a small fraction by mass of the atmosphere, (about 10^{-3}), diffusion will be rapid at the low gas pressures and high temperatures of a stellar atmosphere. Thus, for the purposes of this study, it was assumed that the rate of grain growth is kinetically controlled. A similar assumption was implicitly made in the derivation of the homogenous rate of nucleation.

Assumption 11: Uniform Grain Velocity and Size

In deriving the conservation equations for the models, it was assumed that the grains were non-interacting and, consequently, would not contribute to the atmospheric pressure. It was also assumed that the radii of the grains could be represented by a local effective value. These two assumptions plus the assumption that the grain particles were large enough that Brownian motion could be ignored, made it possible to assign a common velocity and temperature as well as a common radius to all grains in each computational cell. Under these assumptions, the growth of the grains will be unaffected by the processes of coalescence and shattering. While it is acknowledged that variations among particle sizes will probably exist in grain-forming regions, the actual spread in grains size should be restricted by grain-grain collisions (Salpeter, 1974b).

Assumption 12: Continuous Fluid Approximation

The grains were assumed to be momentum coupled to the gas, and the gas to be internally momentum coupled. These two conditions ensure that the momentum absorbed by the grains from the radiation field is uniformly diffused throughout the gas. The assumption of momentum coupling is equivalent to the assumption that the gas and the grains can be treated as continuous fluids with the usual macroscopic properties of flow velocity, temperature, and density, and that their flow can be described by the ordinary equations of hydrodynamics.

Implicitly, the use of the continuous fluid approximation for the grains makes the assumption that the radii of the grains are very small, and their number in each computational cell is relatively large.

The continuum assumption for the grains might be questioned when grain nuclei are just beginning to form. However, nucleation is negligible until the critical supersaturation ratio is reached. Then, nucleation proceeds very rapidly. Thus, the number density of the grains is either so low that they may be neglected or large enough that the continuum assumption is valid. It was predicted that the intermediate state would be passed through so quickly, that its effects would be quickly damped out and could be ignored. This prediction was subsequently confirmed. The use of continuum variables for the gas implies that a kind of "smoothing" process is in effect since the gas velocity and temperature may vary strongly in the neighbourhood of a grain that is moving through the gas and exchanging energy with it. However, all variables will be calculated for volumes large enough to contain many grains to ensure the validity of the continuum assumption for the grains, so this smoothing process for the gas should also be valid.

Assumption 13: Grain Temperature

It was assumed that the grains and the gas had the same temperature as the local radiation field. Lucy (1976) used the same assumption in his study. The adoption of Assumptions 3, 4, 6 and 13 greatly simplified the procedures required to calculate the temperature distribution in the models.

(b) Mathematical Description of the Model

The flow of a gas-grain mixture in a stellar atmosphere is described by two sets of coupled equations: one set pertaining to the gas, and the other, to the grains. The coupling is provided by the transfer of mass and momentum between the grains and gas. Since the atmosphere at some point is free of grains, the homogeneous nucleation of grain nuclei as well as their growth and decay will be included in the process of mass exchange between the two phases. In this respect, the treatment of the problem differs from that of conventional treatments of condensing vapours (see, for example, Marble, 1969).

(i) Continuum Conservation Equations

To describe the flow of a gas, part of which is condensing to form grains, seven conservation equations are required: three describe the conservation of mass, and two each, the conservation of momentum and energy. In Eulerian form, the equations of mass conservation for a spherically symmetric geometry are:

$$\frac{\partial \rho_v}{\partial t} + \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \rho_v u) = - \dot{M}_p \quad (\text{III-3})$$

$$\frac{\partial \rho}{\partial t} + \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \rho u) = - \dot{M}_p \quad (\text{III-4})$$

and

$$\frac{\partial \rho_p}{\partial t} + \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \rho_p u_p) = \dot{M}_p \quad (\text{III-5})$$

where ρ_v , ρ and ρ_p are the densities of the condensing vapour, the total gas component of the atmosphere, and the grains, u and u_p are the velocities of the gas and grains, and $\dot{M}_p$ is the local mass rate of grain formation. $\dot{M}_p$ includes both the process of homogeneous nucleation and the processes of grain growth and decay as a result of condensation and sublimation. The first of the above equations is the conservation of mass equation for the carbon vapour alone, the second, for the total gaseous component of the atmosphere, and the third, the mass conservation for the grains. Implicit in this form of the mass equations is the assumption that the volume occupied by the grains is negligible. Except possibly for hydrogen-deficient stars, this condition should be valid for all late-type stars.

In the absence of grains, the atmosphere is assumed to be in hydrostatic equilibrium. As the grains form and grow, radiation pressure tends to push the grains outward. The movement of the grains through the gas, in turn, tends to drag the gas outward as well. Both of these effects plus the force of gravity must be included in the equations of motion for the gas and grains. Thus, the appropriate conservation of momentum equations are:

$$\begin{aligned} \frac{\partial(\rho u)}{\partial t} + \frac{1}{r^2} \frac{\partial(r^2 \rho u^2)}{\partial r} + \frac{\partial P}{\partial r} \\ = F_p + R - \rho g(r) - \dot{M}_p u \end{aligned} \quad (\text{III-6})$$

and

$$\begin{aligned} \frac{\partial(\rho_p u_p)}{\partial t} + \frac{1}{r^2} \frac{\partial(r^2 \rho_p u_p)}{\partial r} \\ = -F_p + R_p - \rho_p g(r) + \dot{M}_p u \end{aligned} \quad (\text{III-7})$$

where F_p represents the drag force exerted on the gas by the particles, R and R_p the radiation pressure exerted on the gas and grains respectively, $g(r) = GM^*/r^2$, and P is the gas pressure.

The term $-\dot{M}_p u$ appearing in the first of these equations is the rate at which momentum is removed from the vapour as a result of the mass exchange between the carbon vapour and graphite grains. Similarly, the rate at which the grains gain momentum as a result of this condensation is $\dot{M}_p u$. In writing these equations, the viscous stress tensor for the gas has been omitted. This quantity should be very small for the hot thin gas characteristic of stellar atmospheres. Note also that the equation of motion for the grains does not contain a term of the form $\partial P / \partial r$ since the drag force associated with the gross pressure gradient is negligible for very small grains. Moreover, the grains were assumed to have no random motion and, therefore, cannot have any pressure associated with them.

The last two equations needed to complete the system of conservation laws are the conservation of energy equations. The energy equation for the gas can be written as

$$\begin{aligned} \frac{\partial}{\partial t} \{ \rho (e + 1/2 u^2) \} + \frac{1}{r^2} \frac{\partial}{\partial r} \{ r^2 \rho u (e + 1/2 u^2 + P/\rho) \} & \quad (\text{III-8}) \\ = u F_p + u R - u \rho g(r) + \rho E(\rho, r) + Q_p + q \end{aligned}$$

where $E(\rho, r)$ is the net heating rate per gram due to radiation, Q_p is the total heat per unit volume transferred from the grains to the gas phase by thermal conduction, q is the rate that heat is transferred by an exchange of mass, and e is the internal

energy of the gas per gram. Similarly, the energy equation for the grains is

$$\begin{aligned} \frac{\partial}{\partial t} \{ \rho_p (e + 1/2 u_p^2) \} + \frac{1}{r^2} \frac{\partial}{\partial r} \{ r^2 \rho_p u_p (e + 1/2 u_p^2) \} \quad (\text{III-9}) \\ = -u_p F_p + u_p R_p - u_p \rho_p g(r) + \rho_p E_p(\rho_p, r) - Q_p + q \end{aligned}$$

However, the constraints imposed by the assumptions of radiative equilibrium, local thermodynamic equilibrium and a grey atmosphere, significantly change the procedures needed to calculate the temperature of the gas. Instead of solving the equation of conservation of energy for e , the internal energy, and using e to calculate the temperature, the temperature can be found directly from the equation (Lucy, 1976)

$$T^*(r) = 0.5 T_*^* \{ 2W(r) + 3\tau_R(r)/2 \} \quad (\text{III-10})$$

where $W(r)$ is the radiation dilution factor, τ_R , the Rosseland mean optical depth adjusted for the stellar curvature (see Lucy, 1976), and T_* , the stellar temperature¹. The usual form for $W(r)$ is

$$W(r) = 1/2 \{ 1 - (1 - (R^*/r)^2)^{0.5} \} \quad r \geq R^* \quad (\text{III-11})$$

¹In an extended atmosphere, the "radius" of the star for any given optical depth varies greatly with frequency. Thus, the terms "photosphere" and "effective temperature" become ambiguous. Accordingly, the photospheric radius, R^* , is defined to be the radius at which τ_R equals $2/3$. $T_* = (L/4 R^{*2} \sigma)^{1/4}$ is the temperature at the photosphere and acts like an effective temperature for the star.

$$= 1/2$$

$$r < R^*$$

The discontinuous nature of this function caused numerical problems when used to compute the time-dependent models. A form for the dilution factor which is continuous and which forces $T(r)$ to equal T^* when $r=R^*$ is

$$W(r) = 1/2 \{ 1 - (1 - (R_{\text{base}}/r)^2)^{0.5} \} / \{ 1 - (1 - R_{\text{base}}/R^*)^2)^{0.5} \} \quad (\text{III-12})$$

where R_{base} is the radius of the lower boundary, or base of the atmosphere. This form gives slightly higher temperatures throughout the atmosphere than does the standard form for $W(r)$, but this effect is minimized as long as the photosphere is close to the base. For example, for $r = 1.062 \times 10^{14}$ cm, $R^* = 5.59 \times 10^{13}$ cm and $R_{\text{base}} = 5.519 \times 10^{13}$ cm, Equation (III-11) gives $W = 0.075$ whereas Equation (III-12) gives $W = 0.086$. The principal advantage of the modified form of $W(r)$ (Equation (III-12)) is that it completely removes the discontinuity at the photosphere while retaining the essential properties of the standard form. The modified form of $W(r)$ was used to calculate the temperature distribution of all the extended models calculated in this study.

Both the energy equation and the temperature equation represent the conservation of energy. The energy equation, Equation (III-8), contains the term, $(1/r)^2 \partial(r^2 u P) / \partial r$, which represents the work done by rising volumes of gas on their surroundings. In cases where this term is large, the gas

temperature may differ from the temperature of the local radiation field. The temperature equation, Equation (III-10), implies that the gas flow is isothermal in the sense that rising volumes of gas instantaneously adjust to the local temperature. Wood (1979), in his study of pulsation and mass loss in Miras, used a temperature equation similar to Equation (III-10). For a fixed T^* , the temperature in isothermal models is a function of W and τ_R only. W , a geometrical factor is time-invariant. For $\tau_R < 10^{-3}$, the temperature is a function primarily of W and is, therefore, almost time invariant as well. At the very surface of the atmosphere, ($\tau_R \approx 10^{-3}$) even opacity increases by factors of 10^3 caused by the formation of grains will not produce significant temperature changes. At depths below the photosphere, the temperature is determined primarily by τ_R and becomes very sensitive to changes in opacity. It is at these depths that the temperature structure of the atmosphere reflects the changes in conditions caused by mass flows and grain formation. In addition, large mass flows at the base can change T^* resulting in a change of the temperature structure throughout the atmosphere.

(ii) Mass Exchange

The total rate at which mass is exchanged between the solid and vapour phases was written as (Fix, 1969)

$$\dot{M}_p = J 4\pi a^3 \rho_s / 3 + N_p 4\pi a^2 \rho_s \sum_{j=1}^3 j \alpha_j (\beta_j - \beta_j^e) \quad (\text{III-13})$$

where

$$J = 2 \left(\sigma / kT \right)^{1/2} N(1) \sum_{j=1}^3 (\alpha_j \beta_j j^2) \exp(-\Delta F^* / kT) \quad (\text{III-14})$$

is the nucleation rate for the grains (see Appendix B). In this equation, $\rho_s = 2.2 \text{ gm/cm}^3$ is the density of graphite, N_p , the number density of the grains, a , the grain radius, $\Omega = 9 \times 10^{-24} \text{ cm}^3$, the volume per carbon atom in graphite, α_j , the sticking coefficients for C, C_2 , and C_3 , $N(1)$ the number density of C, and ΔF^* is the free energy of forming a grain nucleus having a radius a^* . Also,

$$\beta_j = P_{vj} / (2\pi m_c j k T)^{1/2}$$

and

$$\beta_j^e = P_{vj}^e / (2\pi m_c j k T)^{1/2}$$

where P_{vj} and P_{vj}^e are the vapour pressures and the saturation vapour pressures of C, C_2 and C_3 . The first term in Equation (III-13) arises from the nucleation of the grains, and the second, from the growth of existing grains. The summation is necessary because carbon forms an associated vapour consisting mainly of C, C_2 and C_3 . The number density equation of the grains is obtained by combining Equation (III-3) with Equation (III-13). The result is

$$\partial N_p / \partial t + r^{-2} \partial (r^2 u_p N_p) / \partial r = J \quad (\text{III-15})$$

(iii) Momentum Exchange

If radiation pressure is to cause significant mass loss, the gas and the grains must be strongly momentum coupled, that is, the momentum that is transferred to the grains from the

radiation field must be efficiently transferred from the grains to the gas molecules. Under these conditions, the radiation pressure force will accelerate the grains outward and the viscous drag force will accelerate the gas. Strong momentum coupling will prevail when the grains are travelling at close to their terminal drift velocity and when that drift velocity is not too large compared to the gas velocity. It is also necessary that the gas be internally coupled for this mass loss to occur so that those gas molecules which directly gain momentum through collisions with the grains quickly distribute it to the rest of the gas. It has already been established that the gas can be treated as a continuum. This implies that it is internally coupled. Once the grains form, momentum coupling is established very quickly (Gilman, 1969).

The appropriate form for the particle drag force, F_p , between the gas and the grains depends upon the Reynolds number and the Mach number for the flow. In the present context, the Reynolds number, Re , can be defined as

$$Re = |u_p - u| a \rho / \eta \quad (III-16)$$

$$\cong 2 |u_p - u| / v_{th}$$

where $\eta \cong \rho a v_{th} / 2$ is the viscosity of the gas, and $v_{th} = (kT / \mu' m_H)^{1/2}$ ($\cong 5 \times 10^5$ cm/sec at 1500 K) is the thermal velocity of the gas. If $|u_p - u|$ is small, $Re < 1$, the flow falls into the linear Stokes regime and the drag force per unit volume is

$$F_p = 6\pi a\eta|u_p - u| \quad (\text{III-17})$$

Under these conditions, the grains are said to be position coupled. For large differential velocities, the drag force no longer varies linearly with the drift velocity, $w = (u_p - u)$, but becomes

$$F_p = N_p \pi a^2 \rho (u_p - u)^2 C_D / 2 \quad (\text{III-18})$$

where C_D is an empirically determined drag coefficient.

The velocity at which the transition from the linear to the quadratic form of the drag force occurs is ill-defined. Wickramasinghe (1972) suggests that the quadratic form be used when $w > v_{th}$, and the linear form, when $w < v_{th}$. Lucy (1976) used the quadratic form for all his steady flow models even when the drift velocity was somewhat lower than the local thermal velocity. In his study, he used $C_D = 2$, which corresponds roughly to a Reynolds number of 3. The intent of the present study is to follow the grains from the time they are formed until they are expelled from the atmosphere or until they are evaporated. Thus, the drift velocities will cover a wide range of values. Accordingly, Wickramasinghe's switching procedure was adopted.

(iv) Gas Opacity

The opacity sources included in the calculation of the Rosseland mean for the gas were those of: (a) free-free absorption by H^- , H_2^- , and He^- , (b) bound-free absorption by H^- ,

(c) Rayleigh scattering by H and H_2 , (d) Thompson scattering by free electrons, and (e) bound-bound absorption by CN. The data compiled by Johnson et. al. (1972) were used to calculate the CN opacity. The contributions from each opacity source were computed for a set of thirty frequencies that covered the range from 3.8 microns^{-1} to $0.035 \text{ microns}^{-1}$. The frequency intervals were chosen partially on the basis of giving a good fit to the CN bands. The Rosseland mean was then computed from these thirty values.

The calculation of the absorption coefficients required the knowledge of the electron pressure and of the abundances of CN, H, H^+ , H_2 and He. These quantities were computed by solving a complicated equation of state for the gas. The first ionization levels of Si, Fe, Mg, Al, Ca, Na, K, Cr and S in addition to those of H, C, N and O were used to calculate the electron pressure. Conditions in N-type stars are such that many molecular species are present. The abundances of these molecules were obtained by solving a large set of coupled dissociation equations. The molecules that were included in these calculations were H_2 , H_2^+ , C_2 , C_3 , CO, CN, HCN, C_2H , C_2H_2 , C_3H , N_2 , O_2 , CH, CH_2 , CH_3 , C_3H , C_3H_2 , C_4 , C_4H , C_4H_2 , C_2N_2 , C_2N , HC_3N , C_2H_3 , C_2H_4 , C_3H_3 and NH. This list included only two molecular species which contain oxygen: O_2 and CO. Unlike M stars where many oxygen-bearing species are present, virtually all of the oxygen present in the atmospheres of carbon-rich stars is locked up in the form of CO. The selection of the molecular species to be included in the equation of state calculations was based upon the calculations done by Tsuji

(1964) for carbon stars. The dissociation constants were calculated from the data in the JANAF tables wherever possible. For the remaining molecules the data given by Tsuji was used.

(v) Grain Opacity

The opacity of the grains was represented by the Rosseland mean. Wherever possible, the extinction coefficient for the grains was found by interpolating in the table of coefficients calculated by Wickramasinghe (1967). For the small radii not covered by this table, the approximate Mie expression given by

$$Q_{\text{ext}}(a, \lambda) = -4(2\pi a/\lambda) \text{Im}\{(m^2-1)/(m^2+2)\} \quad (\text{III-19})$$

was used to calculate the extinction, Q_{ext} . In this equation, a is the grain nucleus, λ , the wavelength and $m = K - 2i\sigma\lambda/c$, the complex refractive index of the grain. This approximate expression for $Q_{\text{ext}}(a, \lambda)$ gives good results provided that $2\pi a/\lambda \ll 1$ where a and λ are expressed in the same units. The values of K and σ were taken from the data compiled by Wickramasinghe (1965). For $\lambda^{-1} < 0.47 \text{ microns}^{-1}$, the approximate extinction coefficient, with $K = 4$ and $2\sigma/c = 10$, was used for all grain radii. The Rosseland mean absorption coefficient was calculated by summing the contributions at the same thirty frequencies used to calculate the Rosseland mean for the gas but using a spectral distribution appropriate for a diluted $T = T^*$ radiation field. This procedure was adopted in view of the fact that the radiation actually intercepted by the grains in the

optically thin upper atmosphere should be characterized by the photospheric temperature rather than the local gas temperature. The opacity of the grains is typically several orders of magnitude greater than that of the gas in the grain-forming regions of late type giants. Therefore, in such regions, the absorption coefficient was put equal to the sum of the Rosseland means for the gas and the grains. The accuracy of this procedure should be at least commensurate with that of the grey assumption.

The radiation pressure force terms were written as

$$R = \kappa L / 4\pi r^2 c \quad (\text{III-20})$$

for the gas, and

$$R_p = \kappa_p L / 4\pi r^2 c \quad (\text{III-21})$$

for the grains, where κ and κ_p are the appropriate Rosseland mean opacities.

Chapter IV

NUMERICAL PROCEDURES

The system of equations developed in the preceding chapters was solved numerically on UBC's Amdahl 470 V6-II computer. The solution of the dynamical portion of the programme was based on the algorithms used by Eilek (1975), and those suggested by Harlow and Amsden (1975) for multiphase flow problems. A description of these solution procedures is contained in this chapter. The numerical techniques were subjected to a number of tests prior to the calculation of the grain-forming models. These tests are summarized in Appendix A.

(a) The Solution Algorithm

Physically, the time-dependent equations describe a non-viscous, compressible, two-phase condensable fluid flow in one space dimension. Mathematically, the equations comprise a system of non-linear, first order, partial differential equations. The Implicit Continuous-Fluid Eulerian (ICE) numerical technique was used to solve this system of equations. The developers of this method, Harlow and Amsden (1968), assert that it is a numerically stable and efficient means of calculating transient fluid flows in all velocity ranges. Of particular importance to this study is the fact that the ICE method can be used to calculate transonic flows. No special techniques are required to handle shock waves. The ICE method is

based upon an implicit, finite-difference approximation to the non-linear equations of hydrodynamics. To start the calculations, an initial model is required. Subsequent models are calculated through a sequence of small but finite time steps. Each model represents the configuration of the atmosphere at some definite time after the start of the calculations.

To calculate the finite difference approximations to the space derivatives appearing in the equations, an Eulerian mesh of computational cells was introduced. All field variables were centered in these cells except the velocities of the grains and the gas. These two variables were centered on the cell boundaries. Throughout the calculations, the values of the cell-centered variables were approximated at the cell boundaries by their logarithmic averages, but the velocities were approximated at the cell centers by their straight means. The typically large range of magnitudes of the cell-centered variables made the first procedure mandatory, whereas the typically limited range of velocities permitted the use of the second. Also, Wood (1979) notes that the use of logarithmic averages for cell centered variables is necessary to ensure that stable solutions are obtained for the hydrodynamic equations in the presence of the external body forces of gravity and radiation pressure.

(i) Variable Depth Steps

The depth variable, r , was replaced by the Eulerian co-ordinate, x , which was defined as

$$x = \alpha + \beta r^\gamma \quad (\text{IV-1})$$

where $x=1,2,3,\dots,s$. α , β , and γ are adjustable parameters, and s is the number of cells used to compute the model. In terms of x , the radial depth step was

$$\begin{aligned} dr &= (r_i^{1-\gamma})dx \\ &= h_i dx \end{aligned} \tag{IV-2}$$

and thus, with $\gamma < 1$, increased with increasing radius. This variation in cell size was useful in reducing the total number of cells needed for the calculations. Small cells were required near the photosphere where the field variables changed rapidly with depth, whereas larger cells were suitable near the surface. Wood (1979) used a similar variable zone spacing to compute his models. The parameters, α , β , and γ were adjusted for each effective temperature to give a suitable grid. α and γ were read into the model. β was calculated as

$$\beta = (x^* - \alpha)/(R^{*\gamma}) \tag{IV-3}$$

where x^* is the value x is to have at the photosphere. Generally, the grid was set up such that $x^* = 6$ or 7 , and $\gamma = -3$. α was adjusted until $x = s$ at $r = R_s$, the radius selected as the upper boundary, or surface, of the model. As an illustration, for $T^* = 2400\text{K}$ and $s = 99$, the parameters used were $\alpha = 120$, $\beta = -1.916 \times 10^{+3}$, and $\gamma = -3$.

(ii) Opacity Tables

The Rosseland mean gas opacity, and the partial pressures of C, C₂, and C₃ were calculated as functions of T and ρ at the beginning of the study, and stored in tables. The tables were calculated for three values of the carbon abundance: C/H = 1.22×10^{-3} , 0.957×10^{-3} , and 0.694×10^{-3} to allow for the effects of the depletion of gaseous carbon in the presence of the graphite grains. A three-way interpolation scheme was designed to compute the values of the absorption coefficient of the gas and the partial pressures of gaseous carbon from the values stored in the tables.

(iii) The Initial Model

The initial models required to begin the calculations of the time dependent models, were calculated assuming hydrostatic equilibrium. The pressure distribution was given by the equation

$$\begin{aligned} dP/dr &= \rho \{ GM^*/r^2 - \kappa L / (4\pi r^2 c) \} \\ &= \rho \{ g(r) - \kappa L / (4\pi r^2 c) \} \end{aligned} \quad (\text{IV-4})$$

The optical depth of the atmosphere was given by the differential equation

$$d \log \tau / dr = - \{ \kappa \rho (R^*/r)^2 \} / 2.302585093 \tau \quad (\text{IV-5})$$

and Equation (III-10) was used to calculate the temperature.

The equations were integrated using the modified Euler method with r (or x) as the independent variable. This integration method uses gradients calculated at the mid-points of the integration grid as does the dynamical programme. As in the dynamic programme, logarithmic averages were used to calculate the variables at these points. This procedure gave better values for the mid-point quantities in situations where the gradients were steep than did the procedure of using straight means.

To start the calculation of these initial models, it was necessary to specify a radius, R , an electron pressure, P_e , and an optical depth, τ_0 , for the stellar surface. The surface value of the optical depth was set at 10^{-10} . The surface radius was adjusted to give a surface temperature of about 1300 K. The surface electron pressure was specified as a function of gravity and temperature by the relationship

$$P_e = C + 0.5 \log(g) - 2.2 \theta \quad (\text{IV-6})$$

where C is a constant whose value was generally found to lie between -3 and -4 . The value of C was adjusted for each model until the inward integration gave $\tau = 2/3$ at $r = R^*$. A similar method of calculating the surface electron pressure was used by Mihalas (1967).

The solutions of the initial, hydrostatic models were iterated until $\Delta P/P < 10^{-6}$ and $\Delta \tau/\tau < 10^{-6}$ at each point. Six to ten iterations per cell were generally required. Great care had to be taken to ensure that the models were accurately in

hydrostatic equilibrium before they were transferred to the dynamic programme. Slight deviations from equilibrium, especially at the base of the atmosphere, generated undesirable relaxation pulses and/or shock waves in the dynamic models. (See Appendix A for examples.) Moreover, the relaxation pulses dissipated very slowly especially in the top half of the atmosphere where the damping forces were very small. In its present state, the hydrostatic programme can generate high temperature (20 000K), constant opacity models which, when run on the dynamic programme in the absence of accelerating forces, develop velocities of less than 10^{-7} cm/sec over integration periods of 10^7 sec. The convergence of the low temperature models was good to one part in 10^4 . This limit was imposed by the interpolation routine used to obtain the gas opacity.

(iv) The Hydrodynamic Equations

The procedure used to calculate the time-dependent models is summarized in Table I. In the first part of the cycle, the grain variables were calculated explicitly. In the second part, the transport of the gas and carbon vapour, and the momentum of both the gas and the grains were calculated in an implicit iteration loop. In the final part of the cycle, the temperature distribution and the density of the carbon vapour were calculated.

The first step in the explicit portion of the cycle was to solve the equation

$$f_{\nu} = N_c \rho_{mc} / \{m_H \mu' (QQS + N_c)\} \quad (\text{IV-7})$$

for N_c^{n+1} , where $N_c = C/H$ is the relative number density of carbon atoms in the gaseous state. In this equation, m_H is the atomic mass of carbon, QQS is the total number of gas particles per hydrogen atom excluding carbon, μ' , is the mean mass per particle of the gas, and ρ_v is the density of carbon vapour remaining in the gas. Knowing N_c^{n+1} and using the temperature calculated in the previous model, it was then possible to obtain the partial pressures, P_{vj} , of C , C_2 , and C_3 from the table calculated for this purpose. Next, the saturated vapour pressures, P_{vj}^e , of C , C_2 , and C_3 , (see, Fix, 1969), and the supersaturation ratio, $S = P_{vj}/P_{vj}^e$, were calculated. Then Equations (B-4) and (III-14) were solved to obtain the size of the grain nuclei, a^{n+1} , and the grain nucleation rate, J^{n+1} . The next step was to solve Equations (III-15) and (III-5) to obtain the advanced number density, N_p^{n+1} , and mass density, ρ_p^{n+1} of the grains. Grain production was considered to be significant only in the region where $N_p > 10^{-16}$. This condition set the lower boundary of the grain forming region in the models. Next, the equation

$$a^{n+1} = \{3\rho_p^{n+1}/(N_p^{n+1}4\pi\rho_s)\}^{1/3} \quad (\text{IV-8})$$

was used to calculate the advanced effective radius of the grains. The final step in this portion of the cycle was to calculate the advanced mass rate of grain formation, $\dot{M}_p^{n+1}$, by solving Equation (III-13).

In the second part of the computational cycle, the various field variables approached their final, updated values

through a series of sweeps through an iteration loop. The first step in this procedure was to find an initial value for the advanced pressure. This was accomplished by solving the second order, implicit, finite difference equation obtained by combining the mass and momentum difference equations for the gas (Eilek, 1975). The ZIP differencing method (Harlow and Amsden, 1968) was used to difference the convective terms in the momentum equations, and the interpolated donor cell method (Harlow and Amsden, 1975) was used to difference the convective terms appearing in the continuity equations. The advanced density, i.e. the density corresponding to the model in the process of being calculated, was eliminated from the pressure equation by introducing an approximate expression for the advanced pressure, $\tilde{P}^{n+1,1}$ given by

$$\tilde{P}_i^{n+1} = P_i^n + C_i^n (\tilde{\rho}_i^{n+1} - \rho_i^n) \quad (\text{IV-9})$$

In this expression, the subscripts refer to the grid points, and the superscripts, to the time steps. This definition of $\tilde{P}^{n+1}$ is valid when changes in the equation of state are determined principally by changes in density. In cases where the temperature or the internal energy changes rapidly, the expression defining $\tilde{P}^{n+1}$ can still be used, but the convergence of the solution will be slow.

¹The tilde quantities are used to represent the field variables of the advanced model during the iteration process since these quantities do not really represent the advanced model until the iteration loop has converged.

The precise value of C_i^* in Equation (IV-9) is not specified theoretically. Rather, it is found by making short test runs with different values for C_i^* . In some problems, the value chosen for C_i^* strongly affects the convergence of the solution. In the case of the present problem, however, convergence seemed to be insensitive to the precise value of C_i^* as long as it was close to P_i/ρ_i . Hence, it was decided to set C_i^* equal to $1.125 \times P_i^*/\rho_i^*$ for all models. Test runs at $T^* = 2400$ K indicated that this value for C_i^* gave the fastest rate of convergence. Eilek (1975) used $C_i^* = 1.5 P_i^*/\rho_i^*$.

The pressure equation along with the appropriate boundary conditions was solved for the pressure throughout the atmosphere. The next step in the solution was to calculate the advanced density from the equation which defines $\tilde{P}^{n+1}$. Finally, the momentum equations were solved simultaneously for the grain and gas velocities.

(v) Iterative Procedures

Having obtained initial values for $\tilde{P}^{n+1}$, $\tilde{\rho}^{n+1}$, $\tilde{u}^{n+1}$ and $\tilde{u}_p^{n+1}$, the next step in the calculation cycle was to check the accuracy of the solution and, if necessary, determine the increment to be added to each field variable for the next sweep through the iteration loop. The continuity equation for the gas component of the atmosphere was used as the basis for determining these increments since it was not explicitly used in the solution algorithm. The procedure was to define a function, g_i , as

$$g_i = (\tilde{\rho}_i^{n+1} - \rho_i^n) - (\rho_i^{n+1} - \rho_i^n) \quad (\text{IV-10})$$

where $(\tilde{\rho}_i^{n+1} - \rho_i^n)$ is the calculated change in density, and $(\rho_i^{n+1} - \rho_i^n)$ is the change in density that actually satisfies the continuity equation. Defined in this way, the function, g_i , is the measure of the accuracy of the density calculation. If $|g_i|/\tilde{\rho}_i > 1.5 \times 10^{-3}$, new values of $\tilde{\rho}_i^{n+1}$ were calculated at all depths by solving the system of equations represented by¹

$$g_i + \sum_j (\partial g_i / \partial \tilde{\rho}_j) \delta \tilde{\rho}_j = 0 \quad i, j = 2, 3, \dots, s-1 \quad (\text{IV-11})$$

The coefficients of this Newton-Raphson style relaxation matrix were obtained by numerically differentiating the continuity equation with respect to all $\tilde{\rho}_i$. $\delta \tilde{\rho}_j$ was set equal to zero at the boundaries.

During the passes through the iteration loop, the temperature was held constant, so changes in pressure and density were related by the relationship

$$(\tilde{P}^{n+1} + \Delta \tilde{P}^{n+1}) = f(\tilde{\rho}^{n+1} + \Delta \rho^{n+1}, T^n, N_c^{n+1}) \quad (\text{IV-12})$$

where the function, f , represents the equation of state. Instead of formally calculating the equation of state each time the pressure was to be incremented, the updated pressure was

¹The over-under relaxation parameter that appears in the usual formulation of the Newton-Raphson method for finding the zeros of a set of equations was put equal to one in this study. Therefore, it has not been written in this equation.

interpolated from a table giving the pressure as a function of ρ , T , and N_c . Occasionally, the pressure had to be adjusted even when $\delta\rho^{n+1}$ was negligible because of the method used to initialize $\tilde{P}^{n+1}$. In such cases, however, the solution converged after just one adjustment of $\tilde{P}^{n+1}$. $\Delta\tilde{P}^{n+1}$ was always put equal to zero at the boundaries.

The last variables to be incremented were the velocities. The increments to the velocities were found by substituting the incremented densities and pressures into the momentum equations and solving again for the velocities. Iterative accumulations of changes to the field variables continued until $|g_i|/\delta\tilde{\rho}_i$ and $|\Delta\tilde{P}_i|/\tilde{P}_i^{n+1}$ were both less than 1.5×10^{-3} in each computational cell. Once these conditions had been met, the changes in the field variables were considered to be sufficiently small that the tilde quantities had converged to their final values for the model.

(vi) Optical Depth

After the iteration loop had converged, the next step in the cycle was to calculate the advanced optical depth and temperature distributions for the atmosphere. The optical depth equation was differenced in exactly the same way as the mass and momentum equations except that an explicit formulation was used.

The integration of the opacity equation in both the hydrostatic and the dynamic programme was complicated by the fact that a density inversion exists near the photosphere in these models. This inversion occurred in exactly the same region that the gradients of the field variables such as P , ρ and T

started to increase rapidly with depth. This density inversion was related to variations in the molecular abundances of CN and H_2 . For the chosen model parameters, the molecular abundance of CN peaks in the region near the photosphere. Above this region, the density of the models decreases rapidly with radius, while the temperature changes very slowly. With the formation of the CN molecule, the opacity, and hence the temperature of the atmosphere begins to increase rapidly inward. The rising temperature triggers a rapid dissociation of the atmospheric molecules, including H_2 . The mean molecular weight of the atmosphere decreases as this dissociation occurs and this initiates the density inversion. Deeper in the atmosphere as other molecules including CN dissociate, the steep temperature gradient is maintained by the opacity of H^- and the region of low density is extended inward to the base of the models.

With the standard grid spacing, the calculated values of the optical depth in the region of the density inversion oscillated between two extremes without showing any sign of converging to a single value even when as many as one hundred iterations were performed. It was found necessary to introduce intermediate grid points to reduce the size of the depth step in this region of the models to attain convergence of the optical depth equation. Generally, eighteen intermediate points per cell were used. The solution was iterated at each intermediate grid point until it converged before the calculation at the next point was begun. If the integration had not converged, a new value for the optical depth was defined as

$$\tau_{i+1} = 0.75\tau_{i+1}'' + 0.25\tau_{i+1}' \quad (\text{IV-13})$$

the temperature was recalculated, and the integration procedure repeated until $\Delta\tau_i/\tau_i < 10^{-6}$. Generally, four to six iterations were required to obtain this degree of accuracy even with the use of the intermediate points. To ensure that the optical depths calculated by both programmes were identical, it was necessary to return and recalculate the optical depths in the hydrostatic programme after the equations had been solved at all depth points. In the hydrostatic programme, the optical depth equation was solved simultaneously with the density equation, whereas in the dynamic programme, the densities were known at all depth points before the optical depth equation was integrated. Before this cycling was introduced, the temperature at the lower boundary calculated by the two programmes could differ by as much as 400 K.

After the advanced temperatures were calculated, the temperature at $\tau = 2/3$ was checked to see if it equalled T^* . If it did not, a new effective temperature was defined as

$$T^* = 0.5(T^* + T(\tau=2/3)) \quad (\text{IV-14})$$

and a new photospheric radius, R^* , was defined as

$$R^* = L/(4\pi\sigma T^{*4})^{0.5} \quad (\text{IV-15})$$

and the calculations of τ and T were repeated until $\Delta T^*/T^* < 10^{-4}$.

(b) Boundary Conditions

A total of three boundary conditions were required to solve the dynamical gas equations: the pressure and optical depth at the surface, and the pressure at the base.¹ However, because of the finite difference scheme adopted, it was also necessary to specify the value of the velocity at the base and the surface of the models.² Additional boundary conditions were required to solve the differential equations governing the formation and growth of the carbon grains.

The boundary conditions had to be defined in such away that the solutions to the equations were unique as well as close approximations to the solutions that would exist in the absence of the artificial boundaries. In particular, the boundary conditions had to be chosen such that they minimized the amplitude of waves reflected from the artificial boundaries. Unfortunately, such transparent boundary conditions for general classes of wave equations are non-local in both space and time, and are not useful for practical calculations, (Engquist, et. al., 1977). Consequently, it was necessary to determine approximate boundary conditions that would minimize reflections. A great deal of research went into developing a set of boundary

¹A discussion of boundary conditions suitable for the ICE method is given in Harlow and Amsden, (1968).

²For an illustration of a similar situation in which extra boundary conditions were required because of the difference scheme used, see Engquist, et. al., (1974). This article also contains a discussion of how to select boundary conditions and of their influence upon the solution of the equations of hydrodynamics.

conditions that satisfied this requirement.

(i) Optical Depth

As noted earlier, the surface optical depth, τ_0 , for the initial models was set equal to 10^{-10} . The inward integration of the optical depth equation converges very rapidly, even with a poor initial value for τ_0 . Since the value of τ_0 cannot be determined analytically, the top two points of the initial model were always discarded before the model was transferred to the dynamical programme to eliminate any possible errors in the optical depth scale. The optical depth of the uppermost point that was retained became the fixed boundary value for the dynamical calculations.

A constant surface optical depth worked very well for grain-free test models but was obviously inappropriate when grains were present. Because of their very large opacity, the formation of graphite grains can increase the optical depth by three to four orders of magnitude. Moreover, the surface optical depth was sensitive to the density of the grains both at and above the surface. Allowance for this sensitivity was made by defining τ_0 in these models as

$$\tau_0 = 10^{-2} K(s) R^{*2} / r(s) \quad (\text{IV-16})$$

In this equation, $K(s)$ is the sum of the Rosseland mean absorption coefficients of the grains and the gas at the surface. This definition of τ_0 implicitly assumes that the grain density above the surface boundary falls off as r^{-2} . Such a

density fall off is physically reasonable and has been assumed by Gilman (1972) and by Salpeter (1974b) as well as other authors when analyzing grain forming atmospheres. In the absence of grains, the definition of τ_0 gives a value for the surface optical depth that is very close to the value transferred from the initial models. In the presence of grains, τ_0 has a value that appears to be a smooth extension of the values one and two steps below the surface.

(ii) Pressure

The boundary conditions established for the second order pressure equation were designed to minimize the generation of reflected pulses at the upper and lower boundaries. The procedure used to establish these boundary conditions was based upon the fact that under certain conditions, the equations of gas dynamics (that is, the equation of continuity, the momentum equation, and the equation of state) can be grouped together and written in the form of the acoustic or wave equation.¹ (See, for example, Polozhiy, 1967.) Assume for the moment that the wave equation is used to determine the displacement of a stretched string from its equilibrium position. Under these circumstances,

¹ This transformation is rigorous only at low flow velocities in the absence of body forces. Also, the transformation is based upon the assumption that changes occur in the gas adiabatically and that the gas obeys the perfect gas law. Since all of these assumptions are violated in the stellar atmospheres that are being modelled here, the pressure equation will have only the general form and characteristics of the wave equation. This was one of the complicating factors in determining suitable boundary conditions.

it is well known that if one end of the string is held rigid, a pulse flowing to that boundary will be perfectly reflected, 180° out of phase with the incident pulse (see, for example, Zel'dovich and Raizer, 1966). At a transparent boundary, in contrast, a pulse travelling along a stretched string will produce no reflected pulse at all but will pass through the boundary completely unchanged. At all other boundaries, part of the pulse will be transmitted or absorbed, and part reflected.

Numerical tests indicated that the dynamic models reacted to imposed boundary conditions in a manner very like the stretched string. The data plotted in Figure 1 show the behaviour of a wave generated by a small density perturbation in an otherwise hydrostatic model. With the base pressure held constant, the pulse was almost perfectly reflected. Waves were similarly reflected at the surface when the pressure at that boundary was kept constant. Tests also indicated that holding the velocity equal to zero at the boundaries also generated reflected waves. An example of such a test is plotted in Figure 2.

In order to simulate transparent boundaries for the dynamic models, therefore, it was necessary to predict the change, ΔP , in the boundary values of the pressure as waves approached the edge of the model. To illustrate how this was done, consider the procedure used at the surface boundary. The first step was to define two standard or reference pressures called PSUR and PSUR1. These two quantities were the pressures that would exist at the surface and at one grid point below the surface if the atmosphere were in hydrostatic equilibrium. These

FIGURES 1 and 2 Boundary Condition Tests

These figures show how the dynamic models reacted to two different boundary conditions. In Figure 1, the gas pressure at the base was held constant. In Figure 2, the gas velocity at the base was held equal to zero. The curves in these figures record the behaviour of the model following a 0.001% increase in the density in the 11th cell. In the configuration shown by the dotted curve, the pulses created by the density perturbation are flowing away from the 11th cell. In the configuration shown by the solid curve, the pulse that was initially flowing towards the base boundary has been reflected with little change in amplitude and is propagating towards the surface.

FIGURE 1 BOUNDARY CONDITION TEST

FIGURE 2 BOUNDARY CONDITION TEST

two reference pressures were set equal to $P(s)$ and $P(s-1)$ in the initial model. The second step in the procedure, was to calculate the advanced surface pressure by putting

$$\tilde{P}_s^{n+1} = PSUR \{1 + (PX2 - PX1)/PX1\} \quad (IV-17)$$

$$= PSUR + \Delta P$$

where

$$PX1 = PSUR + (c^n(s) + u^n(s)) \quad (IV-18)$$

$$x(PSUR1 - PSUR)\Delta t/\Delta r$$

$$PX2 = P^n(s) + (c^n(s) + u^n(s)) \quad (IV-19)$$

$$x(P^n(s-1) - P^n(s))\Delta t/\Delta r$$

and

$$\Delta P = PSUR\{(PX2 - PX1)/PX1\} \quad (IV-20)$$

Defined in this way, $PX2$ is the pressure at that downstream point on the wave in the n^{th} model which will be propagated to the surface by the $n+1^{st}$ model. The difference, $PX2 - PX1$, represents the size of the pulse that is superimposed upon the equilibrium pressure structure at this same point. A pulse of this same magnitude, (i.e., ΔP) but scaled by the factor, $PSUR/PX1$, to allow for the decrease in density in the atmosphere, is then added to $PSUR$, the equilibrium surface

pressure in the $n+1^{st}$ model, to get the required value for $\tilde{P}_3^{n+1}$. Thus the effect of the approaching wave is taken into account by adjusting the surface pressure by an amount equal to ΔP .

The above procedure allows for the pressure variations at the surface boundary arising from approaching waves and thereby prevents the generation of reflected pulses. However, it does not allow for the structural changes in the atmosphere that accompany mass flows, nor for the structural changes that accompany the formation of graphite grains. These changes were incorporated into the definitions of both PSUR and PSUR1 by putting

$$\begin{aligned} \text{PSUR}^{n+1} = & \text{PSUR}^n + \Delta t[(1-\Phi)\{u_3^n (u_3^n \dot{M}_{p3}^n - F_{p3}^n)\} \\ & + \Phi\{u_3^{n+1} \dot{M}_{p3}^{n+1} - F_{p3}^{n+1}\}] \\ & - \frac{\Delta t \Delta r}{r_s^2} [(1-\Phi) \dot{M}_{p3}^n (GM^* - \frac{K_3^n L}{4\pi c}) \\ & + \Phi \dot{M}_{p3}^{n+1} (GM^* - \frac{K_3^{n+1} L}{4\pi c})] \end{aligned} \quad (\text{IV-21})$$

and

$$\begin{aligned} \text{PSUR1}^{n+1} = & \text{PSUR1}^n + \Delta t[(1-\Phi)\{u_{s-1}^n (u_{s-1}^n \dot{M}_{p_{s-1}}^n - F_{p_{s-1}}^n)\} \\ & + \Phi\{u_{s-1}^{n+1} (u_{s-1}^{n+1} \dot{M}_{p_{s-1}}^{n+1} - F_{p_{s-1}}^{n+1})\}] \\ & - \frac{\Delta t \Delta r}{r_{s-1}^2} \{ (1-\Phi) \dot{M}_{p_{s-1}}^n (GM^* - \frac{K_{s-1}^n L}{4\pi c}) \\ & + \Phi \dot{M}_{p_{s-1}}^{n+1} (GM^* - \frac{K_{s-1}^{n+1} L}{4\pi c}) \} \end{aligned} \quad (\text{IV-22})$$

where K is the Rosseland mean absorption coefficient for the gas

only, F_p is the drag force, and ϕ is the relative time centering coefficient used to difference the momentum equation. The base reference pressures, P_{BASE} and P_{BASE1} , were adjusted in a similar manner. These adjustments ensure that the reference pressures retain their original relationship to one another. Specifically, the differences $(P_{SUR1} - P_{SUR})/\Delta r$, and $(P_{BASE} - P_{BASE1})/\Delta r$, satisfy the equation of hydrostatic equilibrium. Physically, these adjustments allow for changes in the projected density above the boundaries.

The term, $\dot{M}_p u$, in these equations, represents the momentum that is transferred to that portion of the carbon vapour that condenses to graphite. The term, F_p , represents the momentum that is transferred to the gas as the grains move through it. The remaining terms allow for the effects of the change in the surface gas density caused by grain formation. Implicit within these adjustments to P_{SUR} and P_{SUR1} is the assumption that the weight of the atmosphere above the surface remains constant. However, some variation in the weight above the surface can be expected to occur, especially in the early stages of grain formation. Some allowance for such changes was made by using $\dot{M}_p(s)$ instead of $\dot{M}_p(s+1/2)$ in the density adjustment term for P_{SUR} . Since the ratio of grains to gas was always small for the models, the grain related adjustments made to P_{SUR} and P_{SUR1} were always several orders of magnitude smaller than those related to the gas dynamics.

(iii) Velocity Boundary Conditions

Only two boundary conditions were systematically

tested for the velocity boundary conditions. One method was to put $u(1)=u(2)$, and $u(s+1)=u(s)$, that is, to assume that $\Delta u/\Delta r=0$ at the boundaries. The other, was to extrapolate the inner velocities to get a surface velocity. Both methods were found to work quite well. Tests indicated that the extrapolation method slightly reduced the amplitude of reflected waves when they were present in some of the earlier tests, but consistently produced surface velocities which appeared to be too large in comparison with the velocities at neighbouring points. Neither method interfered with the stabilizing of perturbed models. Since the two methods differed so little, it was decided to use the simpler method of putting $u(1) = u(2)$ and $u(s+1) = u(s)$. A similar procedure was suggested by Harlow and Amsden (1968) for continuation boundaries for both the MAC and ICE methods.

(iv) Boundary Conditions for the Grain Equations

Four partial differential equations, Equation (IV-7), (III-15), (III-5) and (III-3) were solved to obtain the grain field variables, N_c , N_p , ρ_p , and ρ_r . For each equation a boundary condition was required. These conditions were specified at the base of the grain region as

$$N_c = C/H \quad (=1.22 \times 10^{-3})$$

$$N_p = 0$$

$$\rho_p = 0$$

and $\rho_v = N_c m_c / (\mu' (QQS + N_c))$

Because of the nature of the difference equations that were used, additional boundary conditions were required to calculate the values of these variables in the surface cell. These additional conditions all had the general form

$$\Delta \log A / \Delta r = \text{constant} \quad (\text{IV-23})$$

where A represents the various grain variables. In addition, N_c was constrained such that $N_c > O/H$. When N_c became equal to O/H , it was assumed that all gaseous carbon remaining in the atmosphere at that point was in the form of CO and was not available for grain formation or growth.

Table I

FLOW CHART FOR THE TIME-DEPENDENT PROGRAMMESection I Explicit Calculation of the Grain Variables

a) Calculate N_c , the relative number density of the gaseous carbon (Equation (IV-7)).

b) Look up the partial pressures and calculate the vapour pressures of C, C_2 , and C_3 .

c) Calculate a^* , the radius of the grain nuclei (Equation (B-4)).

d) Calculate J, the grain nucleation rate (Equation (III-14)).

e) Calculate the density, ρ_p , and number density, N_p , of the grains (Equations (III-5) and (III-15)).

f) Calculate the average grain radius, a (Equation (IV-8)).

g) Calculate the mass rate of grain formation, $\dot{M}_p$ (Equation (III-13)).

Section II Implicit Solution of the Dynamic Equations

a) Initialize the advanced pressure, $\tilde{P}$ (Equation (A-4)).

b) Calculate an initial value for the advanced density (Equation (IV-9)).

c) Solve the two momentum equations (Equations (III-6) and (III-7)) simultaneously to find initial values for gas and grain velocities, $\tilde{u}$ and $\tilde{u}_p$.

d) Check the solution accuracy of the continuity equation and increment $\tilde{\rho}$ if necessary (Equation (IV-11)).

e) Check the solution accuracy of the equation of state and increment $\tilde{P}$ if necessary (Equation (IV-12)).

f) If either $\tilde{\rho}$ or $\tilde{P}$ were incremented, return to c to increment $\tilde{u}$ and $\tilde{u}_p$.

g) Repeat c, d, e, and f until convergence is obtained at all levels.

Section III Explicit Calculation of the Temperature

a) Calculate the optical depth distribution (Equation (IV-5)).

b) Calculate the temperature of the gas and grains.

c) Calculate the advanced carbon vapour density, (Equation (III-3)). Iterate this solution until convergence is obtained.

d) Store the model and prepare for the next cycle.

Chapter V

RESULTS

Two time-dependent models were calculated, one with $T^* = 2500$ K, and the other with $T^* = 2400$ K. These models will be referred to as model 1 and model 2 respectively. For both of these models, $M = 1.5M_{\odot}$ and $M_{bol} = -6$ (which corresponds to $L = 1.94 \times 10^4 L_{\odot}$). A total of 3600 time steps with $\Delta t \approx 8 \times 10^4$ sec were required to generate model 1, and 4800 time steps with $\Delta t \approx 1.25 \times 10^5$ sec, to generate model 2. Each time step required approximately 3 seconds of computer time. Table II gives some of the physical parameters of these models at the photosphere (R^*, P^* , etc.), at the sonic point (S_c , etc.), and at the surface of the models (T_s , etc.). The subscript, c, denoting the sonic point, is used as a reminder that the condensation of the grains becomes significant at this level in the atmosphere. The sonic point marks the base of what will be called the grain-forming region of the atmosphere in the remainder of this study. The symbols appearing in Table II that have not yet been defined are: $\eta = (r(\tau=10^{-3}) - R^*)/R^*$, the atmospheric extension expressed as a percentage, D , the column density of the grains, Δm , the optical thickness of the grains, and P_d , the pulsation period.

(a) Initial Time-Dependent Behaviour of the Models

The time-dependent behaviour of the two models is summarized in Figures 3 and 4. Initially, the two models

TABLE II

Properties of the Time-Dependent Models		
	Model 1	Model 2
<u>Photosphere¹</u>		
T^*	2500	2400
$\log P^*$	2.67	2.90
$R^*/R_{\odot}$	740	803
$\log g^*$	-1.12	-1.20
v_{esc}	27.8	26.7
$\eta(\tau = 10^{-3})$	7.6%	7.7%
<u>Sonic Point</u>		
T_c	1400	1436
$\log P_c$	-6.14	-5.05
R_c/R^*	1.83	1.58
$\tilde{\tau}_c$	5.42(-5)	1.15(-3)
S_c	5.3	5.1
v_c	2.8	2.9
w_c	14.65	3.2
a_c^*	5.57(-8)	5.57(-8)
a_c	5.65(-8)	5.64(-8)

.....continued

TABLE II (Continued)

Properties of the Time-Dependent Models		
	Model 1	Model 2
<u>Surface</u>		
T_s	1257	1316
$\log P_s$	-6.95	-5.85
R_s/R^*	2.24	1.86
τ_s	4.69(-6)	1.79(-4)
S_s	7.51	6.66
v_s	12.94	14.25
Δv_s	0.0	0.8
w_s	28.49	8.43
a_s^*	5.15(-8)	5.22(-8)
a_s	5.53(-8)	5.51(-8)
C/O_s	1.17	1.24
a_{max}	1.6(-7)	1.6(-6)
D	1.6(-7)	3.4(-6)
$\Delta m(\lambda = 0.7\mu)$	5.0(-3)	1.0(-1)
$\delta \Delta m(\lambda = 0.7\mu)$	-	1.8(-2)
P_d	-	6.48(7)
dM/dt	6.2(-9)	7.4(-8)

¹Cgs units are used throughout except that velocities are in km/sec and dM/dt is in solar masses/year.

exhibited similar characteristics. Both were initiated as grain-free, hydrostatic models. In both, the carbon vapour in the surface layers was highly supersaturated. $S_s = 16.0$ in model 1 and $S_s = 11.9$ in model 2. Test runs indicated that the dynamical response of the atmosphere to the sudden formation of grains in the upper layers would be the generation of a massive outward flow of the whole atmosphere. (See Lucy, 1976). However, the conditions necessary for sudden grain formation throughout the surface layers are probably not physically realizable. In addition, the time required for the model to relax from this artificial impulse is long, and the computer costs required to follow the model while it is relaxing are very high. For these reasons, the rate of grain nucleation was artificially reduced in the initial stages of both models by setting

$$J(t,r) = \alpha(t)J(r) \quad (V-1)$$

where $J(r)$ is obtained from Equation (III-14), and $\alpha^n(t) = \alpha^{n-1}(t) + 4.0 \times 10^{-8} \Delta t^n$ if $\alpha^{n-1}(t) < 1$, otherwise, $\alpha^n(t) = 1$. By controlling the value of $J(t,r)$ in this manner, the adjustment of the atmosphere to the presence of the grains was spread over a time interval of 10^7 sec and the effect on the dynamical properties of the models was much less catastrophic than would have been the case if uncontrolled grain nucleation in the highly supersaturated atmosphere had been permitted to occur.

The dynamical effects of the initial burst of grain formation are best illustrated in Figure 3 where the velocity at the base of model 1 is plotted as a function of time. As Lucy

FIGURE 3 Model 1

The data plotted in this figure are the gas velocity at the surface (upper curve), the optical depth at the sonic point (middle curve), and the gas velocity at the base of the model (lower curve). The pulsation amplitude of each of these variables diminished as the model approached a steady-state. The mass loss rate for this model was $6.2 \times 10^{-9} M_{\odot}/\text{yr}$.

FIGURE 3 MODEL 1

FIGURE 4 Model 2

The data plotted in this figure are the gas velocity at the surface (upper curve), the optical depth at the sonic point (middle curve), and the gas velocity at the base of the model (lower curve). Initially, the pulsation of the base and the sonic point were out of phase leading to the distortions evident in the three curves at the points labelled (b) and (c). After an elapsed time of 30×10^7 sec, a steady pulsation with a period of 6.48×10^7 sec was established. The average mass loss rate for this model was $7.4 \times 10^{-8} M_{\odot}/\text{yr}$.

FIGURE 4A MODEL 2

FIGURE 4B MODEL 2

(1976) noted in the discussion of his static models, the addition of the grain absorption to the optical depth of the atmosphere gives a higher temperature in the grain-free regions at a given pressure than that obtained for the grain-free, hydrostatic initial model. Or, conversely, one may regard the effect of the grains as that of lowering the pressure required to maintain hydrostatic equilibrium at a given temperature. The atmosphere adjusts to this lower pressure requirement by moving mass upwards. This process produced the first pulse in the surface velocity shown in Figure 3. The remaining pulses are relaxation pulses that were generated as the atmosphere adjusted to a new equilibrium state. The initial outward pulse generated by the formation of grains in the atmosphere is also evident in Figure 4 for model 2 but the subsequent behaviour of this model was much different from that of model 1. This behaviour will be discussed in section (b).

In both models, the surface layers accelerated rapidly to very high velocities reaching a peak velocity of 28.0 km/sec at $t = 4.5 \times 10^6$ sec in model 1, and 25.5 km/sec at $t = 7.4 \times 10^6$ sec, in model 2. These velocities decayed relatively slowly to 12.0 km/sec and 13.8 km/sec respectively. The acceleration of the grains was much greater than that of the gas in both models. The grains reached a peak velocity of 113.2 km/sec at $t = 1.6 \times 10^6$ sec in model 1, and 39.3 km/sec at $t = 6.0 \times 10^6$ sec in model 2.

Even with the rate of nucleation artificially reduced, grain formation was very rapid in the initial stages of the models. Grain formation reduced the carbon vapour

supersaturation to an "equilibrium" value close to 5.0 within 10^4 sec of the start of the model calculations. The supersaturation remained close to this equilibrium value throughout the remainder of the model calculations. This initial burst of grain formation in the carbon-rich atmosphere resulted in a period of close to 10^4 sec in which the grain density and, consequently, the driving force on the upper atmosphere, were relatively high. However, the rapid outward flow of the grains relative to the gas, plus the rapid depletion of the free carbon vapour caused by their formation quickly resulted in a reduction of the density of the grains formed in the initial burst. Formation of new grains was controlled by the rate at which carbon-rich material flowed into the grain-forming region. This process resulted in a much reduced grain density ($\rho_p/\rho = 8.7 \times 10^{-4}$ as compared with $\rho_p/\rho = 2.1 \times 10^{-3}$) and, consequently, a weaker coupling between the grains and the gas, lower gas flow velocities and higher drift velocities in both models. (See Table II). These properties are reflected in the deceleration of the surface flow velocities at the points labelled (a) in Figures 3 and 4.

(b) Subsequent Time-Dependent Behaviour of the Models

Both models entered their second dynamic phase near $t = 3 \times 10^7$ sec. This phase was characterized by a small amplitude pulsation which was superimposed upon the outward flow of mass from the atmosphere. In model 1, the pulses were very steady and had an initial amplitude of 0.6 km/sec but they decayed rapidly, and by $t = 27 \times 10^7$ sec, the model had relaxed to almost a steady-

state flow (see Figure 3). In contrast, the pulses in model 2 were initially very irregular, but by $t = 27 \times 10^7$ sec the model had relaxed into a steady pulsation mode with a pulse amplitude of 0.8 km/sec (see Figure 4). In both models, the pulsation had a period of about 750 days (6.48×10^7 sec). Each pulse took approximately 750 days to reach the sonic point of the atmosphere and a further 170 days to reach the surface.

The difference between the dynamical characteristics of the two time-dependent models was evident below the grain-forming region as well as at the surface of the models. An examination of Figure 4 shows that the base of model 2 initially appeared to be relaxing in a manner similar to the relaxation of the base of model 1. However, the small peak at $t = 10 \times 10^7$ sec, the large amplitude pulse centered at $t = 15 \times 10^7$ sec, and the distorted peak centered at $t = 27 \times 10^7$ sec, were all indications that the base pulsations were being driven, and that the driving force was not initially in phase with the pulsations. After $t = 30 \times 10^7$ sec, the pulses at the base became very uniform and showed no evidence of decaying. The constancy of the pulses was also an indication that they were being driven. Each pulse originating at the base of the model could be followed as it propagated with increasing amplitude towards the surface. For example, Figure 5 shows the velocity structure of model 2 at $t = 36.6 \times 10^7$ sec and again at $t = 40.0 \times 10^7$ sec exactly half a period later.

The time-dependence of τ_c , the optical depth at the sonic point, of models 1 and 2 is plotted in Figures 3 and 4. These figures demonstrate the degree of variability of the model

FIGURE 5 Velocity Distribution

The two curves show $v(r)$ at times separated by exactly half of the pulsation period for model 2. The bump at the photosphere in both curves is produced by the presence of the density inversion just below the photosphere. Note that the vertical axis in this figure is $|v|\log(|v|)/v$.

FIGURE 5 VELOCITY DISTRIBUTION

parameters at the base of the grain-forming regions. The uniform pulsations observed at the surface and the base of model 2 as illustrated by the velocity in Figure 4 was found to be characteristic of all the variables throughout the atmosphere in this model.

(c) Mass Loss Rates

The mass loss rate for model 1 after it had relaxed to a steady flow was $6.2 \times 10^{-9} M_{\odot}/\text{yr}$. The average rate of mass loss from model 2 was $7.4 \times 10^{-8} M_{\odot}/\text{yr}$. Both of these rates are almost two orders of magnitude lower than those calculated by Lucy (1976) on the basis of steady-state models but lie within the observational limits for M stars, $2 \times 10^{-9} M_{\odot}/\text{yr}$ to $3.8 \times 10^{-5} M_{\odot}/\text{yr}$, (Sanner, 1976). The only carbon-rich stars for which mass loss rates have been determined from observational data are extreme infrared objects such as CRL 2688 (Lo and Bechis, 1976) and IRC +10216 (Kwan and Hill, 1977) which have very large mass loss rates ($\sim 1.0 \times 10^{-5} M_{\odot}/\text{yr}$). However, Morris et al, (1979) have suggested that the mass loss mechanism in long-period variables is independent of stellar type or C/O ratio and independent of the composition of the grains so it is possible that the range of mass loss rates for N-type stars encompasses the same range as that observed for M-type stars.

(d) Grain Size

The effective grain radius, a , remained close to the critical radius a^* , at all levels in the grain-forming region.

This result was a direct consequence of the very low gas pressure in the grain-forming region of both models. (See Table II). Under such conditions, grain growth is exceedingly slow (see Equation (B-27)). Furthermore, it was found that a^* varied very little throughout the grain-forming region in both models. For example, in model 2, $a^* = 5.57 \times 10^{-8}$ cm at the sonic point and 5.19×10^{-8} cm at the surface, while the effective grain radius at these two points was 5.63×10^{-8} cm and 5.51×10^{-8} cm respectively. Graphite grains of this size contain about 75 carbon atoms. ($N = 4 a^3 / 3 \bar{v}$, $\bar{v} = 9 \times 10^{-24}$ cm³).

While it was not possible to follow each group of grains that formed at each time step as an individual group, it was possible to isolate those particles which formed throughout the grain-forming region at an arbitrary time step and to follow the details of their movement and growth until they escaped from the surface of the atmosphere. The result of such a procedure is shown in Figure 6. The distribution of grain sizes was strongly skewed towards the small end of the spectrum both when the grains were formed, and when they left the atmosphere. However, the distributions show that those grains that form fairly deep in the atmosphere with $a^* = 7.8 \times 10^{-8}$ cm, can succeed in growing to relatively large radii (designated by $a_{\max}$ in Table II) and would, therefore, contain a significant proportion of the mass of the grains were they not formed in such small numbers. The number density of grains was greatest at the sonic point of the atmospheres. The relative number density of the largest grains plotted in Figure 6 to the number density at the sonic point is 10^5 smaller than the relative masses of the grains at these two

FIGURE 6 Grain Size Distribution

This curve shows the size distribution of the grains leaving the surface of the model. For $a > 5.5 \times 10^{-8}$ cm the curves can be approximately fitted by the function $N_p(a) \propto a^{-1.7}$.

FIGURE 6 GRAIN SIZE DISTRIBUTION

points. Thus, the use of an effective radius to represent the size of all the grains at a given level in the atmosphere appeared to be an acceptable approximation of the actual size distribution.

(e) Supersaturation

The formation of the graphite grains only partly reduced the supersaturation ratio of the carbon vapour in the grain-forming regions of the models. In model 1, the carbon vapour supersaturation was reduced from its initial value of 16.0 to 7.5 at the surface, and from 6.4 to 5.4 at the sonic point. In model 2, the corresponding reductions were from 11.9 to 6.6, and from 5.5 to 5.1. No significant graphite formation occurred at supersaturation ratios less than 5.0. For example, in model 2, at $t = 53.5 \times 10^7$ sec, the number density of the grains was $1.6 \times 10^{-4}/\text{cm}^3$ at the level where $S = 4.0$, whereas the number density was $27.0/\text{cm}^3$ two depth steps higher in the atmosphere where $S = 5.1$.

(f) Drift Velocity

The drift velocity of the grains was large in both models (29.0 km/sec and 8.5 km/sec at the surface) implying that the grains were momentum coupled to the gas but not position coupled. One important consequence of the high drift velocities was that the total carbon (gas plus grains) present in any layer of the grain-forming region was less than that implied by a C/O ratio of 1.76, i.e., since carbon was leaving the atmosphere

faster than the rest of the stellar material, the surface layers were being differentially depleted of carbon. The drift velocities were not so large, however, as to imply serious grain damage by sputtering (Salpeter, 1977).

(g) Optical Thickness of the Grains

Assuming that ρ_p varies as r^{-2} , D , the column density of the grains, was 1.6×10^{-7} gm/cm² for model 1, and 3.4×10^{-6} gm/cm² for model 2. These densities correspond to an optical thickness in the grains at $\lambda = 0.7\mu$ of 5.0×10^{-3} and 1.0×10^{-1} respectively. In model 2, the pulsations produced a variation, $\delta\Delta_m$, in the optical thickness of the grains of 1.8×10^{-2} at $\lambda = 0.7\mu$.

Chapter VI

DISCUSSION AND CONCLUSIONS

The results presented in the previous chapter confirm the hypothesis that radiation pressure acting on graphite grains can generate mass flows in carbon-rich red giants and that the resultant mass loss rates lie in the range obtained from observational data. In model 1, where the grain density was low, the flow that was generated eventually relaxed to a steady-state. In model 2, the grain density was a factor of 20 higher and a steadily pulsating flow was generated. This flow took on some of the characteristics associated with small amplitude, long-period, variable carbon stars. The behaviour of the two models will be discussed in this chapter. Following this discussion, some of the assumptions listed in Chapter III will be examined to estimate their probable effects on the models. This chapter will conclude with a presentation of the major conclusions of the study.

(a) Time-dependent Models Versus Steady State Models

The parameters used to calculate model 1 ($T^* = 2500$ K) were chosen to make a direct comparison between it and two of Lucy's (1976) steady-state models possible. The properties of these three models are summarized in Table III. The essential differences between the two modelling approaches were that Lucy assumed (a) that the outflow of the gas and the grains was time-

TABLE III

Properties of the Time-Dependent and Time-Independent Models			
	Time-Dependent	Time-Independent	
<u>Photosphere¹</u>			
T^*	2500	2500	2500
$R^*/R_{\odot}$	740	740	740
$\log P^*$	2.67	2.29	2.44
$L^*/L_{\odot}$	1.94(4)	1.94(4)	1.94(4)
C/O	1.76	1.76	1.76
$M^*/M_{\odot}$	1.5	1.5	1.5
<u>Sonic Point</u>			
T_c	1400	1660	1585
$\log P_c$	-6.14	-3.37	-3.90
R_c/R^*	1.83	1.43	1.45
S_c	5.3	2.0	3.5
τ_c	5.42(-5)	6.0(-2)	2.0(-2)
v_c	2.8	3.2	3.2
a_c	5.65(-8)	1.0(-6)	1.0(-6)

...continued

TABLE III (Continued)

Properties of the Time-Dependent and Time-Independent Models			
	Time-Dependent	Time-Independent	
<u>"Surface" ²</u>			
T_s	1257	1349	1318
$\log P_s$	-6.95	-4.93	-5.44
R_s/R^*	2.24	1.90	1.94
a_s	5.53(-8)	1.0(-6)	1.0(-6)
a_{max}	1.6(-7)	1.0(-6)	1.0(-6)
v_s	12.94	39.1	37.8
w_s	28.49	7.8	13.2
δ_s^3	5.0	8.6	8.2
D	1.6(-7)	2.6(-2)	8.4(-3)
$\Delta m(\lambda = 0.7\mu)$	5.0(-3)	3.62	1.18
dM/dt	6.2(-9)	1.4(-6)	4.4(-7)

¹Cgs units are used throughout except that the velocities are in km/sec and dM/dt is in solar masses/year.

²The point at which $v^2 = 1/2v_{ter}^2$ has been designated as the surface of Lucy's models for the purpose of this comparison.

³ $\delta = KL/4\pi GMc$.

independent, (b) that grain formation occurred only at the sonic point, (c) that all carbon not contained in CO existed in the form of graphite grains above the sonic point, (d) that the grains all had a radius of 1×10^{-6} cm, and (f) that the critical supersaturation ratio, S^* , necessary for the formation of graphite grains in the atmosphere was 2.0 in his model #2, and 3.5 in his model #5. None of these assumption were used in the calculation of the time-dependent model. From an examination of the data given in Table III, it is clear that Lucy's assumptions have a profound influence upon the calculated properties of the expanding atmosphere. However, Lucy's key assumption, that the mass flow is time-invariant, was, in fact, verified at 2500 K. This result was somewhat fortuitous. If the comparison between the two modelling approaches had been undertaken at a lower effective temperature, the assumption of a steady flow would not have been validated.

The most significant difference between the time-dependent and the steady-state models is the calculated rate of mass loss. Salpeter (1974b) has argued that in the case of a radiation-pressure-driven flow, $dM/dt \propto \tau_c$. This relationship is approximately satisfied by both the steady-state and the time-dependent models. Thus, the question of why the mass loss rates differ is basically one of determining why τ_c is so much smaller in the time-dependent model than it was in the steady-state models. Lucy's assumption that S^* is either 2.0 or 3.5 determined the location of the sonic point in his models. In the time-dependent model, in contrast, no assumptions were made as to the value of S^* . Instead, the equations governing the

nucleation and growth of the grains were solved explicitly at each time step and the sonic point was determined by the response of the atmosphere to the presence of the graphite grains.¹ With this procedure, it was found that the sonic point always occurred just above the level where S was 5.0. At this level, both τ_c and the mass density of carbon vapour available to form graphite grains were about two orders of magnitude smaller than the corresponding quantities at the sonic point in both of Lucy's models. Further, only a small fraction of the carbon vapour that was available at the sonic point in model 1 actually was incorporated into the graphite grains. Both of these factors lowered τ_c and, consequently, dM/dt in the time-dependent model.

(b) Uniform Grain Size

It was observed that in both time-dependent models, a and a^* varied very little with depth in the atmosphere. This result can be best understood by considering the following sequence of steps. Assume that at a given radius, r , in the grain-forming region, the atmosphere consists of carbon vapour, graphite grains and an inert gas. Assume also, that $S(r) > 1$ but that $S(r) < S^*(r)$. Under these conditions, the only process by which the carbon vapour can be reduced is by the growth of graphite grains. At the very low densities which prevailed in

¹As is demonstrated in the next section, the form of the nucleation equation as well as the value adopted for σ both influence the location of the sonic point.

the grain-forming region, this growth is almost negligible ($da/dt \cong 10^{-15}$ cm/sec). Thus, $S(r)$ will remain close to, but just slightly less than, $S^*(r)$ until the layer under consideration moves upward to a region of lower temperature. At this new radius, r' , $S(r') > S^*(r')$ and the grain nucleation will proceed to reduce the carbon vapour until $S(r') < S^*(r')$. This process of short "bursts" of grain formation will be repeated continuously as the layer moves outward. The rate at which the nuclei are formed is controlled by the outward flow rate of the atmosphere, but all nuclei are formed in a vapour whose supersaturation ratio just exceeds the local value of S^* . Since both S^* and T were slowly varying functions of depth in the upper layers of the atmosphere after the first burst of grain formation, the radii of the grain nuclei were almost independent of the level at which they were formed. The low rate of grain growth accounted for the fact that, except for the few grains formed well below the sonic point, the grains were only slightly larger than the nuclei.

(c) Pulsation Mechanism

The force driving the pulses in model 2 was traced to an opacity controlled feedback mechanism operating between the hydrogen dissociation zone and the grain-forming region. Under the assumptions used in this study, $T = T(r, \tau)$ and $\tilde{\tau}_{th} = 0$. Consequently, variations in the opacity of the model at a particular level were manifested as immediate changes in the temperature structure at all lower levels. However, since the atmospheric opacity was a function of temperature, an increase

in temperature produced an increase in the local gas opacity which, in turn, increased the temperature of the gas still more. For example, at the sonic point in model 2, $\Delta\tau_c = 2 \times 10^{-4}$ ($\Delta\tau/\tau = 17\%$). This variation had increased to $\Delta\tau = 5 \times 10^{-1}$ ($\Delta\tau/\tau = 3\%$) at the base of the model. Above the photosphere, the small variations in τ had little effect on the structure of the atmosphere, but in the hydrogen dissociation zone, the temperature structure was very sensitive to changes in τ . For example, with $\Delta\tau_c = 2 \times 10^{-4}$, ΔT was 11 K at the photosphere and 20 K near the base of the hydrogen dissociation zone. The resultant shift in the dissociation equilibrium of H_2 increased P by 0.1% and generated an outgoing compression pulse. Similarly, a decrease in τ generated an outgoing rarefaction pulse.

As noted in Chapter V, N_p was almost negligible below the sonic point whereas, above it, N_p was almost constant with depth. It was also at this point that the absorption due to the grains and the fractional changes in the optical depth due to variations in N_p were the largest. With the arrival of a compression wave from the base of the atmosphere, the gas density at the sonic point increases and generates an increase in the grain nucleation and growth rates at that level. The increase in grain production has two consequences. The first, as can be inferred from the discussion in section (a), is to increase the rate of mass loss from the surface. The second, is to increase the optical depth throughout the region below the sonic point and to generate a new compression pulse in the hydrogen dissociation zone. The rarefaction following the

compression has just the opposite effect at the sonic point, depressing rather than stimulating grain production by decreasing the local gas density. Thus, the pulses generated at the base of the atmosphere modulate the grain production rate throughout the grain-forming region of the atmosphere. These changes, in turn, generate new pulses at the base and complete the feedback loop.

The feedback mechanism appears capable of maintaining radial pulsations provided that $\Delta\tau_c \geq 1 \times 10^{-4}$. In the case of model 1, τ_c was small ($\approx 5.5 \times 10^{-5}$) and there was little feedback between the sonic point and the base. This fact is seen most clearly by examining the behaviour of the base of the atmosphere. After the initial large pulse, the base velocity showed no sign of forced oscillations but displayed a series of characteristic relaxation oscillations of decreasing amplitude. Each pulse had less effect at the surface than the previous one as can be seen by examining the behaviour of the surface velocity as given in Figure 3. Eventually the flow approached a steady-state in this model.

The effect of the feedback mechanism was much different in model 2. In this case, the arrival of the first compression pulse at the sonic point increased the optical depth there by $\Delta\tau_c = 6 \times 10^{-4}$ as is shown in Figure 4. The fluctuation of τ_c was not initially in phase with the relaxation oscillations that were commencing at the base, and, consequently counteracted the base pulsations. (See Figure 4). However, after 3 periods, the driving mechanism had forced the base to shift into phase with the fluctuations in the grain-forming region whereafter a

nearly constant amplitude, atmospheric pulsation was maintained for 4 periods.

The interaction between the base and the sonic point is seen most clearly at points (a) (as discussed in Chapter V), and (b) and (c) in Figure 4. At point (b), the pulse that was generated at the base of the atmosphere during the initial stages of the model had reached the sonic point and stimulated an increase in grain formation. The increase in τ_c , in turn, counteracted the relaxation pulse at the base of the atmosphere. The irregular pattern of the pulse originating at the base at point (b) generated the irregular pattern in the variation of τ_c at point (c), which, in turn, affected the characteristics of the base pulse being driven then. Eventually, these irregularities died out and the pulses assumed a regular pattern.

(d) Discussion of the Assumptions

(i) Radiative Equilibrium

The assumption that the atmosphere was everywhere in radiative equilibrium implied that the thermal time scale was zero and that $T = T(r, \tau)$. The important consequence of adopting this assumption was that it implies that the gas was completely coupled to the radiation field and that changes in the model structure could be instantaneously reflected in temperature changes elsewhere in the atmosphere. Implicit in this assumption, is the assumption that energy sources other than the radiation field were negligible. Specifically, the effects of

adiabatic cooling of the expanding atmosphere, the kinetic energy of the flow and the H_2 dissociation energy were all neglected on the basis that all of these energy sources were small relative to the luminosity. For example, the energy change accompanying the dissociation of H_2 in model 2 was estimated to be approximately 1% of the total thermal energy of the gas. However, the relaxation of the radiative equilibrium assumption may have several important consequences. First, a thermal time lag between the changes in τ_c and the dissociation of H_2 may be established. Second, the amplitude of the waves generated in the H_2 zone may be diminished since changes in the internal energy of the layer will tend to counteract any thermal variation in the zone. Third, adiabatic cooling in the surface layers may tend to magnify the amplitude of the pulses somewhat. Tentatively, it seems likely that the relaxation of this assumption will suppress but not eliminate the pulse driving mechanism.

(ii) The Grey Assumption

The predominant effect of assuming a grey opacity was that the surface temperatures of both models were probably several hundred degrees too high for the chosen values of T^* . This estimate was derived as follows. The surface temperature of a grey, plane parallel model is determined by the function $T/T^* = 0.81$. For blanketed, plane parallel models of a solar composition, Tsuji (1976) finds that $T_o/T^* \approx 0.76$ for $T^* < 4000$ K where T_o is the temperature at $\tau = 10^{-3}$. For a blanketed spherical model of similar composition and

$T^* = 2800$ K, Watanabe and Kodaira (1979) obtain $T_o = 1800$ K, or about 300 K lower than the temperature obtained from Tsuji's relationship (i.e., $T_o/T^* = 0.61$), and 600 K lower than that which would be given by a grey, plane parallel model. For both of the time-dependent models, $W \approx 3.15 \times 10^{-1}$ at $\tau = 10^{-3}$ which gives a ratio of $T_o/T^* \approx 0.75$ or about the same surface temperature as Tsuji's plane parallel, blanketed models. Thus, if the surface cooling effects in carbon-rich and oxygen-rich stars are similar, blanketed spherical models of carbon-rich stars should be about 200 K to 300 K cooler than the spherical grey models. The fact that the $T^* = 3400$ K, blanketed, carbon star models of Querci and Querci (1975) and the equivalent solar abundance models of Tsuji (1978) have nearly identical surface temperatures, gives some credibility to the above argument. However, since it was not possible to make a direct comparison between grey and blanketed spherical models of carbon-rich stars, only the direction of the temperature shift should be taken as reliable. On the other hand, Watanabe and Kodaira (1979) find that the surface temperature in their $T^* = 2800$ K model is rather insensitive to large variations (3% to 17%) in the atmospheric extension. If such a trend persisted to even lower temperatures, it is possible that the error in the surface temperature of the grey models is lower than the estimated 200 K to 300 K.

An increase in the effective temperature of the two models would bring them closer to the center of Richer's (1980) luminosity distribution for N stars in the LMC. Mass loss rates obtained from blanketed models at 2500 K and 2400 K would likely

be one to two orders of magnitude larger than the ones obtained with the grey models provided that the temperature of the grain nuclei can be approximated by the ambient gas temperature. (See section (vi)).

(iii) Convective Stability

Although convection has been demonstrated to carry a very small fraction of the energy flux in the atmospheres of red giants (Auman, 1969), convective motions could have several important consequences on the behaviour of the grain-forming atmospheres. (1) The formation of large convection cells suggested by Härm and Schwarzschild (1975) could lead to a "lumpy" grain distribution (Salpeter, 1977). Grains should form preferentially above the upwelling regions at radii larger than the radiative models predict. If it is assumed that the cells have a higher temperature and a lower density than the surrounding gas, then the grains formed in the cell would have a larger radius but a smaller growth rate than the convectively stable models predict. Since the effect of neither of these factors would be very large, the size distribution of the grains would be virtually unaffected by the presence of convection provided that the radiation pressure force acting on the grains was sufficient to prevent them from being dragged back into the photospheric layers of the star by the convective circulation. If the grains do circulate back to the inner atmospheric region, one of two possible processes can be expected to occur. Either the grain will be partially or totally destroyed by evaporation, or, the growth rate of the grain will be greatly enhanced if it

enters a region in which the ambient gas density is high and the carbon vapour abundance has not been seriously depleted by grain formation. Under both of these conditions, the grain-size distribution would be affected to a significant degree. In the first case, the local C/O ratio would be raised and this, in turn, would enhance the formation of grains when convection once again lifted the element to the surface. In the second case, the number density of large grains (10^{-5} cm to 10^{-6} cm) would be greatly enhanced and that of small grains, reduced, bringing the size distribution of the grains into closer agreement with that which has been suggested as giving the best fit to the extinction by interstellar grains of mixed composition (Mathis et al, 1977).

(2) In regions where the convective energy flux is not negligible, the temperature distribution becomes partially decoupled from the optical depth of the region. Under these conditions, the feedback mechanism operating in model 2 would become less efficient or, perhaps, be damped completely even if the convection did not extend higher than the H_2 dissociation zone. Conversely, if the gas remains strongly coupled to the radiation field in the hydrogen ionization zone, the possibility of generating pulses in this zone arises.

(3) A third effect that convection could have on the models is the generation of acoustical waves in the atmosphere leading to the formation of a hot stellar chromosphere. A hot chromosphere would tend to evaporate the grains. It is possible that the infrared emissivity of the small graphite grains is sufficient to prevent the formation of a chromosphere by cooling

the expanding shell as rapidly as acoustical energy is deposited within it.

(iv) Grain Composition

The morphology of stellar and interstellar carbon grains has been the subject of much debate. Czyzak and Santiago (1973) have argued that such grains cannot have a structure like that of graphite on the grounds that (1) the temperature and pressure conditions required for grain nucleation to be possible will yield only highly disordered carbon grains, and (2) the crystallization of these disordered grains requires higher temperatures and/or pressures than the grains are likely to encounter. However, Stephens (1980) has shown that disordered amorphous or glassy carbon grains with radii $\geq 5 \times 10^{-7}$ cm have a UV extinction peak that is red-shifted relative to the 2200 Å peak in the interstellar reddening curve. He also has shown that the UV extinction peak for carbon grains shifts towards the violet as the degree of crystallinity increases and/or the grain size is decreased. In his study, Stephens interpreted this data as indicating that interstellar carbon grains are more likely to have a structure resembling that of graphite than of amorphous carbon and it is tempting to use this same argument as a justification of the assumption of the formation of graphite grains in the models. However, Stephen's conclusion is not necessarily valid if the grains are smaller than 5×10^{-7} cm as was the case in both time-dependent models. Indeed, the existence of the extinction peak at 2200 Å may be interpreted as suggesting that interstellar carbon grains have radii $\leq 10^{-7}$ cm.

The values of the surface-free-energy, σ , the Lothe-Pound factor, and the optical constants used to calculate the grain opacity were all derived from the assumption that the carbon grains had the structure of graphite. The adopted value of σ (1000 ergs/cm²) has been suggested as a representative value for graphite (Tabak et al, 1975). However, the uncertainty associated with choosing this value for σ is large enough that it should be as representative of nuclei of amorphous carbon solids as it is of graphite particles.

The appropriate form of the Lothe-Pound replacement factor for carbon structures other than graphite has not been determined (Tabak, et al, 1975). If the grains are, in fact, amorphous in structure, Γ could have been in error by several orders of magnitude without seriously changing the dynamic behaviour of the models.

(v) Lothe-Pound Nucleation Theory

Tabak et al, (1975) have argued that the Lothe-Pound form of the nucleation equation should be applicable to the formation of graphite grains. They state that the uncertainties regarding the specific structure of the grains and the choice of an appropriate value for σ should outweigh the uncertainties inherent in the use of the Lothe-Pound theory. They note also, that nucleation experiments on non-polar materials give results that are in good agreement with the predictions of the Lothe-Pound theory. More recently, Draine (1979) has seriously questioned the validity of the Lothe-Pound theory especially in

the case of the nucleation of very small clusters ($N^* \leq 20$), where N^* is the number of carbon atoms per critical nucleus. While his objections do not at first appear to apply to the present study since it was found that $N^* \cong 70$, it was still possible that the use of the Lothe-Pound theory may have resulted in an erroneous nucleation rate. As an alternative to the Lothe-Pound theory, Draine suggests that for the nucleation of atomic solids, the surface-free-energy should be replaced by $\sigma/2$ where σ is the surface-free-energy of the bulk solid, and that Γ be set equal to 1. To compare these two different descriptions of the nucleation of small grains, consider the nucleation rate given by each when $T = 1446$ K, $S = 5.0$, and $P_{\text{at}} = 1.4 \times 10^{-11}$ dynes/cm². Under these conditions, the Lothe-Pound theory gives $a^* = 5.6 \times 10^{-8}$ cm, and $\Gamma = 5 \times 10^{29}$. Γ^{-1} is comparable to the exponential term in the rate equation, $\exp(-\Delta F^*/kT) = 2.3 \times 10^{-29}$. The Lothe-Pound nucleation rate, $J(\text{LP}, \sigma=1000)$, is equal to 8.6×10^{-6} sec and is essentially given by the remaining pre-exponential terms in Equation (III-14). When Draine's suggested nucleation rate equation is used, a^* is reduced to 2.8×10^{-8} cm, $N^* = 10$, $\exp(-\Delta F^*/kT) = 2 \times 10^{-4}$, and the nucleation rate, $J(\text{D}, \sigma/2=500)$, is reduced to 4×10^{-10} sec⁻¹. On the basis of this comparison, it would appear that the Lothe-Pound theory overestimates the nucleation rate. However, in his analysis, Draine assumed that $\sigma = 1400$ ergs/cm² for spherical carbon grains. Using this value for σ and the same values for T , S and P_{at} as above, Γ becomes 6×10^{30} , $a^* = 7.8 \times 10^{-8}$ cm, $\exp(-\Delta F^*/kT) = 3 \times 10^{-29}$, $N^* = 220$, and $J(\text{LP}, \sigma=1400)$ is reduced to $\sim 3 \times 10^{-56}$ sec⁻¹. In this case, reducing σ to $\sigma/2$, and assuming

$\Gamma' = 1$, reduces the exponential term to 10^{-10} and increases the nucleation rate by a factor of 10^{41} to $J(D, \sigma/2=700) = 10^{-15} \text{ sec}^{-1}$. Thus, the nucleation rate is much more sensitive to the chosen value of σ than it is to the use of the Lothe-Pound theory. This result is similar to that reached by Deguchi (1980) who found that the number density of silicate grains formed in steady flows was insensitive to the form of the nucleation equation. When σ is large, J is also extremely sensitive to the value of $\ln(S)$ appearing in the exponential term of the nucleation equation. For example, an increase in S to 9.5 (a factor of 1.9) is all that is required to increase $J(LP, \sigma=1400)$ to $J(D, \sigma/2=700)$.

A comparison between the two rate equations cannot be restricted to comparing only the values of the term $\Gamma \exp(-\Delta F^*/kT)$. If, for example, $\Gamma' = 10^{-5} \Gamma$ had been used to "correct" $J(LP)$ such that $J(LP, \sigma=1000) = J(D, \sigma/2=500)$, the base of the grain forming region would have been shifted from $S_c \cong 5.0$ to $\cong 5.9$ in the models and the mass loss rate would have been decreased in model 2 by about 15%. Also, the effective grain radius would have been equal to $a = 5 \times 10^{-8} \text{ cm}$. If, instead, $J(D, \sigma/2=500)$ had been used to obtain J , the effective grain radii in both models would have been reduced to $a = 2.8 \times 10^{-8} \text{ cm}$ and the sensitivity of J to $\ln(S)$ would have been considerably reduced since in this case $\exp(-\Delta F^*/kT) \rightarrow 1$. For example, for the case under consideration, increasing S by a factor of 2 would increase the exponential term only by a factor of $\sim 10^2$. However, the pre-exponential term contains the factor $(P_{\infty}/T)^2$ and this term varies strongly with depth in the

atmosphere with the result that $J(D, \sigma/2=500)$ at $T = 1513$ K, $S = 3.5$ is comparable to $J(D, \sigma/2=500)$ at $T = 1446$, $S = 5.0$. Thus, while $J(D, \sigma/2=500) < J(LP, \sigma=1000)$, the use of $J(D)$ would have moved the base of the grain-forming region deeper into the atmosphere so that the overall effect of using the Lothe-Pound theory may have been to underestimate the mass loss rate of the two models and to overestimate the radii of the grain nuclei.

(vi) Grain Temperature

The temperature of both graphite and amorphous carbon smoke is elevated above the equivalent black body temperature by the greenhouse effect. This fact was ignored when it was assumed that the gas and grains had the same local temperature. Using the Mie theory with the optical constants of graphite, the vibrational temperature of the grains can be obtained by solving the energy balance equation

$$4\pi a^2 \{ \bar{Q}_p(a, T^*) W \sigma T^{*4} + n (2kT/\pi \mu' m_H)^{0.5} \alpha k (T - T_p) \} \\ = 4\pi a^2 \bar{Q}_p(a, T_p) \quad (V-1)$$

In this equation, $\bar{Q}_p$ is the Plank mean extinction coefficient for the grains, n , the number density of the gas particles, and α , the accommodation coefficient. Under conditions representative of the grain-forming regions of the two models, it was found that the collisional term was negligible compared with the radiational heating term, i.e., the grains were not thermally coupled to the gas. As a consequence of this non-LTE effect, it was estimated that the vibrational temperature of the

grains could be elevated by as much as 150 K above the temperature of the ambient gas. This temperature difference is likely an upper limit for the following reasons. (1) The Mie theory may not give valid results for grains with radii $\approx 5 \times 10^{-8}$ cm (Draine, 1981a). (2) The grains probably have lattice defects which could increase their infrared emissivity and decrease their temperature. (3) Morphologically, the grains may resemble amorphous carbon smoke particles more closely than they do graphite particles and empirically, carbon smoke particles have been found to have a much smaller greenhouse effect than graphite particles (Draine, 1981b). (4) In a non-grey atmosphere, J_ν , the mean intensity, and B_ν , the Planck function, may differ by a large amount so that the grain absorption term appearing in the above equation may be overestimated.

If the greenhouse effect also elevates the temperature of the unstable clusters by 150 K, then grain nucleation in both models would have been prevented. In this case, the fact that carbon grains appear to form in carbon-rich red giants suggests two alternative hypotheses: either (1) $\Delta T \leq 150$ K for atmospheric carbon particles, or (2) the carbon condenses on a nucleus of some other material. SiC has been suggested as a likely candidate for the seed nuclei (see, for example, Draine, 1981a) since it has an inverse greenhouse effect and, initially, the grains would be cooler than the ambient gas. The hypothesis of SiC seeding is consistent with the fact that those carbon stars having an infrared excess appear also to have the 11.2μ absorption feature that has been attributed to absorption by SiC.

grains. However, if the temperature difference between the grains and the gas is established after the grains are formed, then, although evaporation would dominate grain growth, the grains with $a = 5 \times 10^{-8}$ cm would be able to escape from the atmosphere before being evaporated.

The possibility that the gas was thermally coupled to the grains was investigated by examining the energy balance equation appropriate for the gas. The heating term of this equation will be dominated by the radiation field provided that

$$n'n < (n'n)_{\text{crit}} = \bar{K}(T^*)W\sigma T^{*4} / \{4\pi a^2 (2kT/\pi\mu'm_H)^{0.5} \epsilon kT\} \quad (\text{VI-2})$$

where n' is the number density of the grains per gram of stellar material. Using the Plank mean for $\bar{K}$ and $W = 0.1$, $T = 1500$ K, $a = 5.5 \times 10^{-8}$ cm and $T^* = 2400$ K, $(n'n)_{\text{crit}} = 8.97 \times 10^{28}$ gm $^{-1}$ cm $^{-3}$, whereas in the grain-forming region of model 2, $n'n = 1.21 \times 10^{25}$ gm $^{-1}$ cm $^{-3}$. If the Rosseland mean is used for $\bar{K}$, $(n'n)_{\text{crit}}$ is reduced to 2.8×10^{26} gm $^{-1}$ cm $^{-3}$. In a non-grey model, the value of $(n'n)_{\text{crit}}$ would probably lie somewhere between these two extremes. It is apparent, therefore, that gas-grain collisions would have been ineffective in heating the gas in the models. At lower temperatures, however, $n'n$ will be larger and the gas may become thermally coupled to the grains. It is also noted that if $J(D)$ is substituted for $J(LP)$, then the grains may form deeper in the atmosphere, $n'n$ will be much larger than that obtained in the present models, and collisional heating of the gas may tend to equilibrate the gas and grain temperatures.

(e) Conclusions

The major conclusions arising from this study are:

1) Radiation pressure acting on grains is a viable mass loss mechanism in cool, carbon-rich red giants. At $T^* = 2500$ K, this mass loss mechanism generated a mass loss rate of $6.2 \times 10^{-9} M_{\odot}/\text{yr}$, and at $T^* = 2400$ K, a mass loss rate of $7.4 \times 10^{-8} M_{\odot}/\text{yr}$.

2) The intrinsic variability of cool, carbon-rich stars may be directly linked to the formation of atmospheric grains. The pulsation of model 2 appeared to be stable with a period of 750 days which is consistent with observed periods of variable carbon stars. The source of the pulses appears to be an opacity controlled feedback loop acting between the grain-forming region of the atmosphere, and the hydrogen dissociation zone.

3) Grains formed in the atmospheres of carbon-rich stars have radii that are $\leq 10^{-7}$ cm. Such grains are much smaller than the silicate grains that appear to be the cause of the interstellar polarization of starlight. However, the computed size of the carbon grains is consistent with (a) the location of the 2200 Å peak in the interstellar extinction curve, (b) the sharp increase in this curve in the UV region, and (c) the fact that the UV extinction is greater in the apparently carbon star rich areas of the LMC than it is in the Milky Way Galaxy (Nandy, et al, 1980).

4) The mass loss rates derived from both steady-state and time-dependent models are very sensitive to the assumptions used in their construction. By assuming that $S_c = 2.0$, Lucy (1976) calculated a mass loss rate of $1.4 \times 10^{-6} M_{\odot}/\text{yr}$, whereas, the

time-dependent model predicts that at $T^* = 2500$ K, $S_c = 5.3$ and $dM/dt = 6.2 \times 10^{-9} M_{\odot}/\text{yr}$. However, the degree of grain formation in the time-dependent models was very dependent upon the form of the nucleation rate equation that was used and the value chosen for σ . This dependency is the major uncertainty associated with the determination of these mass loss rates.

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Appendix A

NUMERICAL TESTS

In the course of its development, the computer programme was subjected to a number of tests to determine its behaviour under specified conditions and to test the stability and accuracy of the solution algorithms. Numerical tests were also made to select optimum values for some of the computation parameters. For all of these tests, the programme was modified to compute model atmospheres of hot, pure hydrogen stars. The only source of opacity included in these models was electron scattering.

(a) Stability tests

(i) Artificial Mass Diffusion and Viscosity

Although the ICE method can handle the propagation of shock waves without the addition of artificial viscosity terms, it is necessary to add some form of artificial dissipation to the system of equations to prevent the development of the numerical instabilities which can occur at the sonic points and stagnation points, (Richtmeyer and Morton, 1967). Such instabilities are produced by the near-discontinuities that result from the very large values of $|\partial u / \partial r|$ that accompany shock transitions. Various forms have been suggested for this term. The form used in this study, was

$$\left(\frac{\partial q}{\partial r}\right) = -\frac{\lambda_j}{h_j \delta x r_j^2} \left\{ \rho_{j+\frac{1}{2}} \left(r_{j+\frac{1}{2}}^2 \frac{u_{j+\frac{1}{2}}}{h_{j+\frac{1}{2}} \delta x} - r_j^2 u_j \right) - \rho_{j-\frac{1}{2}} \left(r_j^2 \frac{u_j}{h_{j-\frac{1}{2}} \delta x} - r_{j-\frac{1}{2}}^2 u_{j-\frac{1}{2}} \right) \right\} \quad (\text{A-1})$$

where

$$\lambda_j = (1/r_j + \delta \rho_j / h_j \delta x) h_j \delta x^2 + (3u_j^2 + (1-2\theta)c^2) \delta t / 2 \quad (\text{A-2})$$

A similar term was added to the momentum equation for the grains. This form of the artificial viscosity term was first suggested by Hirt (1968) for quasilinear equations and was used by Eilek (1975) in the dynamical study of Seyfert galaxies. Although this form of $\partial q / \partial r$ does not necessarily equal zero in steady flows, test runs indicated that it does become negligible under steady flow conditions in comparison with the other terms in the momentum equation. Moreover, near shock transitions, Hirt's form of $\partial q / \partial r$ is very sensitive to the velocity gradient, $\partial u / \partial r$, and, consequently, is very effective in damping numerical shock perturbations.

In some applications of the ICE method, an artificial mass diffusion term, ζ , is added to the continuity equation to further stabilize the equations. Eilek (1975) and Wood (1979), for example, used such a term. However, test runs indicated that the use of such a term actually distorted the results of these calculations rather than stabilizing them. For this reason, a mass diffusion was not included in the calculations.

The models proved to be quite sensitive to the value of the artificial viscosity coefficient. Test runs using a

perturbed model were made with $\lambda_i = \lambda_{max}$, $0.1\lambda_{max}$ and $10\lambda_{max}$, where λ_{max} represents the maximum value of the artificial viscosity coefficient calculated for the model (Eqn. (A-2)). These tests clearly showed that values of λ_i that are too large can introduce instabilities into the solution rather than removing those generated by other means, while putting $\lambda_i = 0.1\lambda_{max}$ resulted in too little stabilization when shock waves were present in the flow. Thus, it was decided to calculate a value for λ_i for each computational cell rather than try to find a constant value of λ_i that could be used to calculate the artificial viscosity term at all points.

(ii) Time Centering

Some of the difference equations used in the programme were written such that they contained both forward and backward time differences. For example, the continuity equation for the gas was written as

$$\begin{aligned} \frac{\rho_i^{n+1} - \rho_i^n}{\Delta t} = & \frac{\theta}{\delta x h_i r_i^2} \{ r_{i-\frac{1}{2}}^2 (\rho u)_{i-\frac{1}{2}}^{n+1} - r_{i+\frac{1}{2}}^2 (\rho u)_{i+\frac{1}{2}}^{n+1} \} \\ & + \frac{(1-\theta)}{\delta x h_i r_i^2} \{ r_{i-\frac{1}{2}}^2 (\rho u)_{i-\frac{1}{2}}^n - r_{i+\frac{1}{2}}^2 (\rho u)_{i+\frac{1}{2}}^n \} \\ & - \theta \dot{M}_{\rho i}^{n+1} - (1-\theta) \dot{M}_{\rho i}^n \end{aligned} \quad (A-3)$$

where θ is the relative time centering constant. A similar constant, ϕ , was used to difference the momentum equations. Thus, the gas momentum equation, (Eqn. (III-6)), was written as

$$\begin{aligned}
\frac{(\rho u)_{i+\frac{1}{2}}^{n+1} - (\rho u)_{i+\frac{1}{2}}^n}{\Delta t} = & \frac{\phi}{h_{i+\frac{1}{2}}\delta x} (\tilde{P}_i - \tilde{P}_{i+1}) + \frac{(1-\phi)(P_i^n - P_{i+1}^n)}{h_{i+\frac{1}{2}}\delta x} \\
& + \phi \{F_{\rho u, i+\frac{1}{2}}^{n+1} - (\dot{M}_{\rho u})_{i+\frac{1}{2}}^n\} \\
& + (1-\phi) \{F_{\rho u, i+\frac{1}{2}}^n - (\dot{M}_{\rho u})_{i+\frac{1}{2}}^n\} + R_{i+\frac{1}{2}}^n
\end{aligned} \tag{A-4}$$

where

$$\begin{aligned}
R_{i+\frac{1}{2}}^n = & \frac{1}{h_{i+\frac{1}{2}}\delta x r_{i+\frac{1}{2}}^2} \{u_{i+\frac{1}{2}}^n (r_i^2 \rho_i^n u_i^n - r_{i+1}^2 \rho_{i+1}^n u_{i+1}^n)\} \\
& - \rho_{i+\frac{1}{2}}^n GM^*/r_{i+\frac{1}{2}}^2 - (\partial q / \partial r)_{i+\frac{1}{2}}
\end{aligned}$$

contains only terms known from the previous cycle. Written in the above forms, the difference equations are stable provided that θ and ϕ lie between 0.5 and 1.0.

Tests were used to choose optimum values for θ and ϕ . Tuchman et. al. (1978) state that the conservation equations are solved most accurately when $\theta = \phi = 0.5$ but because of stability considerations, they actually used $\theta = \phi = 0.6$ in their calculations. In the present study, the choice of $\theta = \phi = 0.6$ also proved to give the best compromise between stability and accuracy. Test runs in which θ and ϕ were set equal to 0.5 developed large instabilities in the velocity profile when the hydrostatic equilibrium of the model was perturbed slightly. The tests in which θ and ϕ were put equal to 0.7 appeared to be "over-stabilized" in the sense that the perturbation pulse that was generated by a slight adjustment to the density distribution was suppressed by the equations.

(iii) The Courant Condition

Tests were used to see whether or not time steps larger than those given by the Courant condition, $\Delta t < \Delta r / |u+c|$, could be used. Two types of tests were performed. The first type was done on unperturbed models, and the second, on perturbed models. For the first test, a model that departed only very slightly from hydrostatic equilibrium was used. This model was followed with the dynamic programme until it reached hydrostatic equilibrium first with Δt equal to $2/3 \Delta t_c$, where Δt_c is the time step given by the Courant condition, and second, with Δt equal to $4/3 \Delta t_c$. After the same elapsed time, the two runs produced models which were indistinguishable.

The test on the perturbed model gave quite different results. For this test Δt was put equal to $2/3 \Delta t_c$ and $2 \Delta t_c$. In the first of these runs, the pulse travelled through the surface without any sign of instability throughout the atmosphere. But in the second run, when the perturbation reached the base of the atmosphere, a series of rapid oscillations were generated. These oscillations grew from -2×10^2 cm/sec to -2×10^6 cm/sec after which the base velocity decreased slowly reaching 1.65×10^6 cm/sec at the end of the run. It was apparent, therefore, that the Courant condition had to be used to determine the maximum size of the time step that could be used for each model.

Because Δt_c depends both upon the speed of sound and the flow velocity, its value can vary appreciably throughout the atmosphere. Accordingly, Δt_c was calculated at each grid point for both the gas and the grain flow velocities, and Δt was set

equal to 0.99 times the minimum value of Δt_c . When shock waves were involved, Δt was put equal to 0.5 times the minimum value of Δt_c as suggested by Richtmeyer and Morton (1967) to ensure that the equations remained stable.

(b) Boundary Condition Tests

The boundary conditions were extensively tested with models whose luminosity was time-dependent. The results of one test of these boundary conditions is shown in Figure (A-1). For this test, the luminosity was initially set at $L=9.0 \times 10^6 L_\odot$, which was just 9% below the stability limit for the star being modelled. This model was perturbed by increasing L by 0.003%. As a result of this perturbation, a pulse was generated at the base of the atmosphere. The data plotted in the figure show the relaxation pulses at the base. No sign of any reflected waves were observed in this and similar tests. The second curve plotted in this figure serves to demonstrate how sensitive the models were to the formulation of the boundary conditions. For this run, the reference pressure, P_{BASE1} , was defined as

$$P_{BASE1}^{n+1} = P_{BASE1}^n + \Delta t \{ (1-\phi) u_2^n \rho_2^n (g_2 - \kappa_2^n L / 4\pi r_2^2 c) \\ + \phi u_2^{n+1} \rho_2^{n+1} (g_2 - \kappa_2^{n+1} L / 4\pi r_2^2 c) \} \quad (A-5)$$

The calculations in this test were extended to $t=6.0 \times 10^6$ sec during which the base velocity showed no sign of stabilizing. The definition of P_{BASE1}^{n+1} was only one of many factors to which the boundary conditions were sensitive. Other factors

FIGURE A-1 Base Velocity of Perturbed Model

This figure shows the sensitivity of the dynamic models to the procedure used to calculate the boundary conditions. The only parameter which was different in the two models plotted in this figure was the reference pressure, P_{BASE1} , used to calculate the pressure boundary condition at the base. Curve (a) shows the time-dependence of the velocity at the base of the model when P_{BASE1} was calculated on the basis of the net loss of mass from the second cell (see Chapter V). After the initial perturbation of the luminosity, this model was relaxing to a steady state. Curve (b) shows the behaviour of the velocity at the base when P_{BASE1} was calculated on the basis of the average mass loss from the second cell (Equation A-5). This model showed no signs of relaxing to a steady state.

FIGURE A-1 BASE VELOCITY OF PERTURBED MODEL

included the definition of C_1^* used in the calculation of $\tilde{P}_1^{**}$, the error tolerances used to check the solution of the equation of state and the continuity condition, and the method of interpolating in the pressures to find the value of Z used in the specification of the boundary pressures. For example, the use of log values for the interpolation procedure generated large, rapid, growing oscillations in the base velocities.

The behaviour of the surface velocities of the high luminosity model is shown in Figure (A-2) and Figure (A-3). The pulse generated at the base of the atmosphere had grown into a shock wave by the time it reached the surface. Again, the first pulse was followed by a series of relaxation pulses. The second figure shows the behaviour of the velocity near the surface during the passage of one of these shock waves. Again, no evidence of reflected waves can be seen in the data.

(c) Luminosity Tests

The ability of the dynamic programme to treat time-dependent problems and shock wave phenomena was extensively tested before the calculation of grain-forming models was initiated. Three types of tests were run. In the first, the stellar luminosity was increased at a constant rate. In the second, the luminosity was fixed at a value just below the Eddington limit and perturbed slightly. In the third test, the stellar luminosity was increased until it exceeded the Eddington stability limit. The computer programme appeared to handle each situation very well.

For the first test, the model parameters were set at

FIGURES A-2 and A-3 Surface Velocity of a Perturbed Model

These figures show the passage of shock waves through the surface of a $T^* = 20\,000\text{ K}$ model. In Figure A-2, six successive shocks of slowly decreasing amplitude are shown. The passage of the fourth of these shock waves through the upper layers of the model is shown in Figure A-3. The curves labelled (a) to (e) show the velocity distribution of the outer layers of the model at successive time intervals. There was no evidence of waves reflected from the surface boundary following the passage of these shocks.

FIGURE A-2 SURFACE VELOCITY OF PERTURBED MODEL

FIGURE A-3 SURFACE VELOCITY

$M^*=30.3M_{\odot}$, $T^*=20\,000\text{K}$, $\log g=4.0$, and $R^*=8.99R_{\odot}$. The extension of the atmosphere was $\Delta g=4.6\%$ which is quite modest compared to that encountered in red giants, but large enough that the model variables covered many orders of magnitude. The density, for example, ranged from $2.2 \times 10^{-6} \text{ gm/cm}^3$ at the base to $2.1 \times 10^{-23} \text{ gm/cm}^3$ at the surface. The starting luminosity for this test was $L=1.179 \times 10^4 L_{\odot}$ and was increased at a rate given by

$$L^{n+1} = L^n (1 + 8 \times 10^{-6} \Delta t) \quad (\text{A-6})$$

This rate increased L by about 10% over one thermal time scale. A run during which L increased by 4% is plotted in Figure (A-4). It is clear from this data that a constant increase in luminosity produces a mass flow of almost constant velocity throughout the entire atmosphere. It also produces an increase in both the effective temperature and the radius of the photosphere. The surface pulses seen in this data are an example of the difficulties that resulted when the initial model was not perfectly hydrostatic. It was after this set of runs, that a variety of methods were incorporated into both programmes to ensure that the hydrostatic programme could produce models in which the condition $|dP/dr - \rho g| < 10^{-10}$ was satisfied throughout the entire atmosphere, and that the dynamic programme could retain such models in hydrostatic equilibrium for prolonged periods in the absence of accelerating forces.

For the second test, the model parameters that were used were $T^*=29\,926\text{K}$, $M^*=30M_{\odot}$, $R^*=35.1R_{\odot}$, $\log g=4.0$ and $\kappa=0.4 \text{ cm}^2/\text{gm}$. The luminosity was set at equal to $0.9L_{\text{crit}}$ where

FIGURE A-4 High Luminosity Model

Over short time periods, a steady increase in the luminosity of a $T^* = 20\,000\text{ K}$ model produced a mass flow of almost constant velocity throughout the lower half of the model. The pulse at the surface of this model was generated by small departures from hydrostatic equilibrium in the initial model. The three curves show the velocity distribution of the model at successive time intervals.

FIGURE A-4 HIGH LUMINOSITY MODEL

$$\begin{aligned}
 L_{\text{crit}} &= (4\pi c G M / \kappa M_{\odot}) L_{\odot} \\
 &= 9.93 \times 10^5 L_{\odot}
 \end{aligned}
 \tag{A-7}$$

is the Eddington stability limit for the atmosphere.¹ Under these conditions, the atmosphere was expected to be very sensitive to small changes in the model parameters. This prediction was tested by increasing the luminosity of the model by 0.003%. Its behaviour was then followed for 1.1×10^7 sec (about 5 dynamical time periods). The luminosity increase first produced a small, outward flow. The greatest acceleration occurred at the base where the pressure perturbation was greatest. This behaviour was followed by a series of decaying oscillations as the programme sought to re-establish hydrostatic equilibrium under dynamically unstable conditions. (See Figure (A-1).) Each oscillation generated a pulse that had become a shock wave by the time it had reached the surface. Near the end of each post-shock period, the infall velocity of the surface material exceeded the speed of sound. Since the surface oscillations appeared to be decaying it was concluded that if the calculations were continued long enough, the surface would eventually stabilize as it had in the previous test. However, because of the slowness with which the model appeared to be stabilizing, the calculation of further models for this test was concluded to be impractical at this time.

For the third luminosity test, the model parameters

¹In the first luminosity test, $\Gamma (=1.179 \times 10^4 L_{\odot} / 9.9 \times 10^5 L_{\odot})$ was equal to 0.01 and the atmosphere was radiationally quite stable.

used were $M^*=30M_{\odot}$, $T^*=20\,000\text{K}$, $L=9\times 10^5 L_{\odot}$, $\log g=2.0$ and $R^*=49R_{\odot}$. This model was also very close to being dynamically unstable ($L/L_{\text{crit}}=0.9$). It was predicted that an increase in the luminosity large enough for it to exceed the Eddington limit would lead to spontaneous mass loss. In addition, it was probable that numerical instabilities related to real physical instabilities might arise (Mihalis, 1978). These predictions were tested by increasing the luminosity in gradual steps until it reached $10.16\times 10^5 L_{\odot}$ ($= 1.02L_{\text{crit}}$). The increase was controlled by the equation

$$L^{n+1} = L^n (1 + \alpha \Delta t) \quad (\text{A-8})$$

where α was increased by 2×10^{-7} for each of the first 35 models, and decreased by the same amount for each of the second 35 models to give a smooth increase in luminosity. After the 70th model, α was put equal to zero, and the resultant behaviour of the model was followed. As expected, the model proved to be quite unstable to mass loss.

The data plotted in Figure (A-5) show the gas velocity for the last model in which the luminosity was increased, and for a model 2×10^4 sec later. As expected, the atmosphere continues to be accelerated outward even when ΔL was equal to zero. For the second of these two models, the velocity was ten times the sound velocity at the base of the atmosphere, and about one-half the sound velocity at the surface. Under these conditions, the data gave no indication of any problems at the sonic point, and the programme seemed perfectly capable of

FIGURE A-5 Perturbed Dynamically Unstable Model.

The luminosity of this model was raised above the Eddington stability limit. After $t = t_1$, the luminosity of the model was kept constant but the atmosphere continued to accelerate outwards.

FIGURE A-5 PERTURBED DYNAMICALLY UNSTABLE MODEL

treating transsonic flows of this type.

The fact that the gas flow did not become steady when ΔL was reduced to zero, was taken to be further evidence that the dynamic programme was working properly. Theoretically, it can be shown that steady transsonic flows cannot be produced or maintained by the condition that $M > 1$ throughout the atmosphere, (Mihalas, 1978). The data plotted in Figure (A-5) show that the whole atmosphere was accelerated outward during the time period covered by this data. The behaviour of this model was followed until $t = 7.85 \times 10^4$ sec. During this interval, the velocity at the base of the atmosphere reached a maximum of 1.6×10^6 cm/sec and then began to decrease slowly. This behaviour generated an outgoing pulse which was propagated at the local speed of sound. For the model at which the calculations were terminated, the velocity of the peak of the pulse was 3.57×10^7 cm/sec. On the basis of the behaviour exhibited by models in other test runs, it was expected that the peak velocity of this pulse would be increased by several more orders of magnitude before it reached the surface. Since no provisions were made in the programme to handle relativistic velocities, the calculations were terminated at this point.

With the completion of these tests, the computer programme was judged to be capable of coping with a wide variety of dynamical problems.

Appendix B

THE NUCLEATION AND GROWTH OF GRAPHITE GRAINS

The classical theory of homogeneous nucleation is based upon the model that the vapour contains clusters of molecules bound together by intermolecular forces. It is assumed that these clusters, A_i , containing (i) molecules, are formed by a single molecule, A_1 , combining with a cluster containing ($i-1$) molecules, A_{i-1} , or, through the evaporation of a single molecule from a cluster, A_{i+1} , containing $i+1$ molecules. Assuming that equilibrium conditions prevail, the concentrations of clusters of various sizes is given by a Boltzmann-like distribution function

$$N(i) = N(1)\exp(-\Delta F_i/kT) \quad (B-1)$$

where $N(i)$ is the number density of the A_i clusters, $N(1)$, the number density of the monomers, (carbon atoms in the case of graphite formation), and ΔF_i , the change in the Helmholtz potential with respect to the free vapour state. The above equation is also known as the law of mass action. ΔF_i may be considered as the free energy of formation of a cluster of i molecules from the vapour state provided that the vapour is maintained at a constant temperature and pressure. Under these conditions, the free energy may be written as

$$\Delta F_i = \sigma a_i i^{2/3} - ikT \ln(S) \quad (B-2)$$

where the supersaturation ratio, S , is the ratio of the pressure of the vapour, P_v , to the equilibrium vapour pressure of the solid, P_v^e , i.e. $S = P_v/P_v^e$, σ is the specific surface-free-energy in ergs/cm², and a_0 is the surface area per surface molecule (Abraham, 1974). An alternate and more useful form for the energy of formation is

$$\Delta F_i = 4\pi a^2 \sigma - (4\pi a^3/3\Omega)kT \ln(S) \quad (B-3)$$

where the cluster containing i molecules is assumed to be spherical with radius a . The molecular volume in the solid state is denoted by $\Omega (=4\pi a^3/3i)$. The first term in this expression for ΔF_i represents the surface-free-energy or "surface tension" of the cluster, and the second term, the contribution made by the bulk-free-energy change. For very small values of i , ΔF_i is positive, whereas for large i , it is negative. Physically, this means that small clusters are unstable and decay rapidly, while large clusters grow spontaneously. For some critical radius, a^* , ΔF_i has a maximum value. The addition of just one more molecule to a nucleus of this critical size decreases the free energy of the cluster and leads to irreversible growth of the grain at the expense of the supersaturated vapour.

For a given temperature and degree of supersaturation, the critical radius is found by differentiating ΔF_i with respect to the radius, a , and setting the derivative equal to zero. This gives

$$a^* = 2\Omega\sigma/(kT \ln(S)) \quad (B-4)$$

This expression for a^* reveals the fundamental relationship between the critical radius and the supersaturation ratio: namely, the larger the supersaturation ratio, the smaller the critical radius. Thus extremely few critical clusters are present to act as nuclei for grain formation until S is quite large.

The free energy of forming a critical size nucleus is

$$\begin{aligned}\Delta F^* &= 4\pi(a^*)^2\sigma - (4\pi(a^*)^3/3)kT\ln(S) \\ &= 4\pi(a^*)^2\sigma/3\end{aligned}\quad (B-5)$$

ΔF^* represents a barrier to the spontaneous growth of grains. Physically, this barrier arises from the formation of an interface between a cluster and the vapour.

The critical reaction in the formation of grains, therefore, is that in which clusters exceed the critical size by the addition of a single molecule. The rate of this critical reaction is called the nucleation rate, J , and is defined as

$$J = \infty CN^* \quad (B-6)$$

where N^* is the equilibrium number density of the critical sized clusters, $C = 0.25N(1)(8kT/\pi m)^{1/2}$ is the collision rate between the vapour molecules and the clusters, and ∞ , the sticking coefficient, is the probability that a colliding molecule will stick to the nucleus. Making the appropriate substitutions yields

$$J = \frac{4\pi(a^*)^2 P N(1) \exp(-\Delta F^*/kT)}{(2\pi m k T)^{0.5}} \quad (B-7)$$

Since the collision rate depends upon the pressure, increasing the pressure and, therefore, the supersaturation ratio, enhances the nucleation rate. However, the main influence of the supersaturation ratio occurs in the determination of ΔF^* . A small change in S changes J by many orders of magnitude.

The above expression of J is the "classical" one and does not include the effects of such processes as tunneling. It is derived from the work of Becker and Döring (1935). Better representations of the nucleation rate incorporate a number of modifications to the classical form. These are described in the following sections.

(a) Non-equilibrium

The use of a Boltzmann-like distribution function for the size distribution of the clusters is accurate only when the conditions for thermodynamic equilibrium prevail. In this case, $\partial N(i)/\partial t = 0$. However, once the clusters exceed the critical size, they are removed from the equilibrium composition of the "cluster gas" and become stable nuclei. This reduction of N^* is allowed for by the introduction of a non-equilibrium factor, Z^* , which is defined as

$$\begin{aligned} Z^* &= [a_0 \sigma / (9\pi k T (i^*)^{4/3})]^{1/2} \\ &= [4\pi (3/4\pi)^{2/3} / (9\pi k T (i^*)^{4/3})]^{1/2} \end{aligned} \quad (B-8)$$

This factor also allows for the fact that clusters having $a > a^*$ have a non-zero probability of evaporating. Normally, Z^* is of the order of 10^{-1} to 10^{-2} . Donn et al. (1965) used $Z^* = 10^{-2}$ as a typical value for graphite. Substituting the above expression for Z^* and using the identity $a_0 = 4\pi(3\eta/4\pi)^{2/3}$, the expression for the nucleation rate becomes

$$J = 2\alpha(\sigma/kT)^{0.5} [\eta P / (2\pi mkT)^{0.5}] N(1) \exp(-\Delta F^*/kT) \quad (B-9)$$

The Zeldovich non-equilibrium factor is important in these calculations because it produces a reduction in the nucleation rate by one to two orders of magnitude. Thus, appreciable nucleation requires somewhat higher supersaturation ratios than those predicted by the classical theory. Note, however, that the exponential term containing the supersaturation ratio is the same in both theories, (compare equations (B-7) and (B-9)), and since this factor dominates the kinetics and the thermodynamics of the nucleation process, only a slight increase in supersaturation is required to offset the effect of the non-equilibrium factor.

(b) Associated Vapours

Thus far, it has been assumed that the condensing vapour is non-associated, with the vapour molecules occurring only as monomers in the absence of clustering. However, it is well known that carbon vapour consists of C, C₂, C₃ and possibly larger molecules. In their investigation of nucleation in associated vapours, Katz et al. (1966) found that association

results in two opposing effects. The first effect is an increase in the condensation rate, and the second (and larger) effect is an increase in the activation barrier. The overall effect is a reduction in the rate of nucleation and, consequently, an increase in the critical supersaturation required for a nucleation rate equal to that in a non-associated vapour.

Assuming that the vapour consists of monomers, dimers and trimers, the nucleation rate for an associated vapour as developed by Katz et. al. is

$$J = 2(\sigma/kT)^{1/2} N(1) \sum_{j=1}^3 (\alpha_j \beta_j j^2) \exp(-\Delta F^*/kT) \quad (B-10)$$

where

$$\beta_j = P_{vj}/(2\pi m_j kT)^{1/2} \quad (B-11)$$

In these expressions, P_{vj} is the partial pressure of the j -mer and α_j , the appropriate sticking coefficient. For carbon vapour, Thorn and Winslow (1957) quote the values $\alpha_1 = 0.37$, $\alpha_2 = 0.34$, and $\alpha_3 = 0.08$. The sum over j increases the nucleation rate - an effect which seems reasonable for associated vapours since the association complexes are indistinguishable from the clusters but, unlike the clusters, the association complexes are stable. However, the important effect of the association is the term P_{vj}/P_{vj}^e used to determine the supersaturation ratio. For non-associated vapours, $S = P_v/P_v^e$, where P_v is the total partial pressure of the vapour and P_v^e is the equilibrium vapour pressure of the solid. If the association is appreciable, $P_{v1}/P_{v1}^e < P_v/P_v^e$

and the activation energy is considerably increased. For example, if the vapour consists almost entirely of dimers, the activation energy barrier, ΔF^* , is the square of the value given by the classical theory for the non-associated vapour. This effect is expected to be quite important when considering the condensation of carbon vapours in stellar atmospheres since Tsuji's (1964) calculations indicate that much of the free carbon is in the form of C_2 and C_3 molecules.

(c) The Lothe-Pound Factor

The classical theory of homogeneous nucleation is based upon the standard postulates of thermodynamics. However, thermodynamic functions are derived for macroscopic systems, and their use in describing the properties of small clusters of molecules is debatable. Nevertheless, the classical Becker-Döring nucleation rate is found to agree well with empirical values for many liquids including that for water. Generally, these liquids are polar, strongly hydrogen-bonded liquids, and have a low surface entropy (Good, 1957). However, Abraham (1974) has suggested that the apparent success of the Becker-Döring theory in predicting the nucleation rate of polar liquids is fortuitous. Certainly it grossly underestimates the nucleation rate of non-polar liquids.

Lothe and Pound (1962) suggested that the failure of the Becker-Döring theory arises because it considers the clusters to be at rest when in fact they form a kind of macro-molecule gas, so that their translation, vibration and rotation must be taken into consideration. This Lothe-Pound correction

increases the nucleation rate by 10 to 20 orders of magnitude (Deguchi, 1980). Using quantum-statistical arguments to calculate the absolute entropy of the clusters, Lothe and Pound deduced that the free energy of formation of the clusters is given by the expression

$$\Delta F_i = 4\pi a^2 \sigma - (4\pi/3) a^3 kT \ln S - kT \ln Z_{\text{trans}} - kT \ln Z_{\text{rot}} - \Delta F_{\text{rep}} \quad (\text{B-12})$$

instead of the expression in Equation (B-3). Z_{trans} and Z_{rot} , the translational and rotational partition functions respectively, are given by

$$Z_{\text{trans}} = (kT/P_{\text{NI}}) (2\pi m_i kT)^{3/2} / h^3 \quad (\text{B-13})$$

where (kT/P_{NI}) is a normalizing factor, and

$$Z_{\text{rot}} = (8\pi^2 I kT)^{3/2} / h^3 \quad (\text{B-14})$$

where $I = (8\pi m a^2) / 15$, is the moment of inertia for spherical clusters.

Lothe and Pound introduced a factor, ΔF_{rep} , called the replacement free energy, to remove some of the error inherent in using thermodynamic functions to describe the properties of the clusters. In their original paper, they argued that six degrees of freedom are needed to energize the cluster. Consequently, six degrees of vibrational freedom in the cluster must be removed from the free energy of the cluster. This is represented by the

term, ΔF_{rep} in Equation (B-12). They approximated this decrease by deactivating one monomer molecule giving

$$\Delta F_{rep} = Ts \quad (B-15)$$

where s , the molecular entropy, is of the order of $5k$ for many liquids. An additional term of $kT \ln(2\pi i)/2$ was suggested to account for the separation of the clusters. Thus, they suggested that

$$\Delta F_{rep} = 5kT + kT \ln(2\pi i)/2 \quad (B-16)$$

As noted by Tabak, et al. (1975), the form Lothe and Pound chose for the replacement free energy has generated much debate. Most of it applies to the appropriate form to use for polar molecules for which the Lothe-Pound theory over-estimates the rate of nucleation. For many non-polar materials, the Lothe-Pound theory worked very well. Moreover, Abraham (1974) has suggested that the Lothe-Pound theory should be applicable to clusters of simple atoms. The Lothe-Pound theory should, therefore, be applicable to the nucleation of graphite grains. Accordingly, it was worthwhile searching for the best possible form for the replacement free energy. Tabak et al. (1975) suggested the form

$$\Delta F_{rep} = kT \ln Z'_{vib} \quad (B-17)$$

where Z'_{vib} is the vibrational partition function of one molecule. Unfortunately, the exact analytical expression for the

partition function for a simple, three-dimensional crystal is not known, so Tabak, et al., (1975) adopted the single molecule partition function of a one-dimensional harmonic oscillator of classical frequency $\nu = k\theta_c/h$ where θ_c is a characteristic temperature. The expression for this partition function is

$$Z'_{\text{vib}} = \exp(-\theta_c/2T) / \{1 - \exp(-\theta_c/T)\} \quad (\text{B-18})$$

At high temperatures, i.e. $T \gg \theta_c$, $Z'_{\text{vib}} = kT/h\nu$. Even when $T \approx \theta_c$, $Z'_{\text{vib}} = kT/h\nu$ is a reasonable approximation. This method of approximating the partition function of crystals is used in the Born-Kármán theory of solids. At low temperatures, this theory is approximated by the Debye theory, and $\theta_c = \theta_D$, the Debye temperature, whereas at high temperatures, the Einstein model is used, and $\theta_c = \theta_E$, the Einstein temperature. Under these conditions, the replacement free energy becomes,¹

$$\Delta F_{\text{rep}} = 6kT \ln(T/\theta_c) \quad (\text{B-19})$$

Physically, the replacement free energy allows for the fact that the total number of internal degrees of freedom for a small cluster of N molecules is $(3N-6)$ not $3N$ as is assumed for large systems in deriving the Helmholtz potential, ΔF of a macroscopically stationary drop. For small systems, the correction, ΔF_{rep} is very important.

¹In their paper, Tabak, et al., (1975) did not include the term $\exp(-\theta_c/2T)$ in their expression for Z'_{vib} .

Recently, normal-mode techniques have been used to approximate the replacement free energy of idealized microcrystallites. Since carbon condenses to a crystal rather than to a liquid drop as has been assumed in the discussion of nucleation up to this point, it is reasonable that these new estimates for ΔF_{rep} should describe carbon nucleation even more accurately than the above equation. For spherical microcrystallites, the exact, normal-mode techniques are approximated very accurately by means of a classical Einstein theory of crystalline solids generalized to apply to the surfaces of microcrystalline clusters (Abraham, 1974). In terms of the Einstein model, the replacement free energy is written as

$$\Delta F_{rep} = -kT \ln \{ i^{1/2} \exp(L) (T/\theta_E)^L \} \quad (B-20)$$

where $L = 7.1$ for spherical micro-crystallites. The Einstein temperature appearing in this equation is related to the Debye temperature by the simple relation (Wilson, 1957)

$$\theta_E = (3/5)^{1/2} \theta_D \quad (B-21)$$

For carbon, $\theta_D = 1850$ K and $\theta_E = 1433$ K. In terms of the Lothe-Pound theory, therefore, the nucleation rate is given by the expression

$$J = \Gamma^2 (\sigma/kT)^{1/2} N(1) \sum_{j=1}^3 (\alpha_j \beta_j j^2) \exp(-\Delta F^*/kT) \quad (B-22)$$

where

$$\begin{aligned} \Gamma &= [Z_{\text{trans}} Z_{\text{rot}} / Z_{\text{vib}}] \\ &= [T^{-3.1} P_{\text{vib}}^{-1} (\theta_E/e)^{7.1} (128\pi^4 m^2 k^2 / 15 h^4)^{3.2} a^{7.5}] \end{aligned} \quad (B-23)$$

is the Lothe-Pound (or statistical weight) factor.

The basic difference between the Becker-Döring and the Lothe-Pound theories is their representation of the total surface-free-energy. Typically, the expression used in the Becker-Döring theory over-estimates the surface-free-energy by greatly over-estimating the number of surface molecules in the droplet. For non-polar liquids, this over-estimate is removed by the Lothe-Pound theory. However, for polar liquids, the Lothe-Pound theory fails to account for important deviations of the surface properties of the critical nucleus from those of the bulk liquid. For these liquids, the Lothe-Pound theory gives the correct nucleation rate only when the surface tension for the clusters is assumed to be about 20% greater than that of the bulk liquid. For graphite formation, such a correction is not expected to be necessary, and the nucleation of graphite grains should follow the Lothe-Pound description.

The choice of an appropriate value for the surface energy of graphite is complicated by its crystal structure. For its basal surface, $\sigma = 40$ to 170 ergs/cm², while for its prism surface, $\sigma = 4000$ to 4800 ergs/cm². Following Tabak et al., (1975) a value of $\sigma = 1000$ ergs/cm² was used for the spherical nuclei that were assumed for the purposes of this study. This

value for σ was also used by Fix (1969) and by Donn et al. (1968).

(d) Condensation

Once the supersaturation ratio, S , reaches its critical value, large numbers of nuclei will form and begin to grow by accretion of free atoms impinging upon their surfaces. At the same time, the evaporation of atoms will decrease the size of the grains. Assuming that the grains are spherical, the net rate of change of the volume of the grain is

$$dV_p/dt = 4\pi a^2 n \sum_{j=1}^3 j \alpha_j (C_j - E_j) \quad (B-24)$$

where V_p is the volume of the grain, and C_j and E_j , the condensation and evaporation fluxes of the j -mer. For grains, the evaporation flux is

$$E_j = P_{vj}^e / (2\pi m_j kT)^{1/2} \quad (B-25)$$

and the condensation flux is

$$C_j = P_{vj} / (2\pi m_j kT)^{1/2} \quad (B-26)$$

Using the fact that $V_p = 4\pi a^3/3$ for spherical grains, the radial growth of the grain can be written as

$$da/dt = n \sum_{j=1}^3 j \alpha_j (C_j - E_j) \quad (B-27)$$

which is independent of the size of the grain.

As the grains grow, they deplete the vapour of the condensing species. This quickly decreases the degree of supersaturation, effectively stopping the nucleation process. Growth of the grains already formed, however, continues until $C_j = E_j$, i.e. until $P_{\omega j} = P_{\omega j}^e$ for all values of j . At the same time, by reducing the partial pressures of the j -mers, the growth of the grains will affect the dissociation equilibrium of the molecules containing atoms of the condensing species. This process must be considered in determining the final size that the grain will obtain. Eventually, of course, a new equilibrium state will be reached in which the presence of the solid material is accounted for.