Pergamon

Planet. Space Sci., Vol. 44, No. 9, pp. 1051–1063, 1996

0032–0633/96 $15.00+0.00

PII: S0032–0633(96)00084–0

A model for the overabundance of methane in the atmospheres of Pluto and Triton

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Received 6 June 1995; revised 6 May 1996; accepted 10 June 1996

Abstract. A model for producing atmospheric CH_4 mixing ratios larger than would be expected from simple vapor pressure equilibrium over a solid solution of N_2 and CH_4 is described. Laboratory experiments show that rapid sublimation of a dilute (0.2% mole fraction) solid solution of CH_4 in α-N_2 produces a residue of nearly pure CH_4 grains. The CH_4 grains begin to form very quickly, and most of the CH_4 originally in solid solution with the N_2 is taken up by the grainy residue rather than sublimating. If the same is true for the much slower sublimation rates on Pluto, patches of nearly pure CH_4 ice grains will be built up on sub-seasonal timescales. Such CH_4 patches will be in contact with Pluto's predominantly N_2 atmosphere. Further sublimation of these patches will be controlled by molecular and turbulent diffusion, as will be the condensation of CH_4 from the atmosphere in other areas. It is shown that the balance between diffusive sublimation and condensation can easily produce 1% mixing ratios of CH_4 in the atmosphere, generally consistent with requirements for explaining Pluto's 100 K upper-atmospheric temperature and producing a steep positive temperature gradient in the 2–3 μb region. The same mechanism can explain Triton's less elevated atmospheric CH_4 mixing ratio. Copyright © 1996 Elsevier Science Ltd

Introduction

With solid N_2 established as the dominant constituent covering the surface of Pluto (Owen *et al.*, 1993), there is no question that N_2 gas is also the dominant constituent of the atmosphere. The vapor pressure of N_2 exceeds that of the other detected volatiles, CO and CH_4, by approximately one order of magnitude and four orders of magnitude, respectively (Brown and Ziegler, 1980). The fact that these species appear to be at least partly in solid solution with the N_2 (Owen *et al.*, 1993; Quirico and Schmitt, 1996) means that their equilibrium pressures in the atmosphere should be even lower than their vapor pressures over the pure solids by a factor equal to their mixing ratio for an ideal solid solution (Raoult's law). According to the scenario of ideal solid solutions, taking the N_2:CO:CH_4 ratio in the ice to be 0.97:0.005:0.026 (*ibid.*) and an ice temperature of 40 K (Tryka *et al.*, 1994), Pluto's atmospheric composition should be $1.0:4.8\times10^{-4}:3.7\times10^{-6}$.

The lightcurves measured using the Kuiper Airborne Observatory (KAO) and at telescopes at Charters Towers, Aukland, Hobart, Toowoomba and Mt. John during the 1988 occultation of a star by Pluto (Hubbard *et al.*, 1989; Elliot *et al.*, 1989; Millis *et al.*, 1993) gave a direct measurement of the ratio of temperature to molecular mass, $T/\mu = 3.54\pm0.29\ \mathrm{K\,amu^{-1}}$ in Pluto's atmosphere (Elliot and Young, 1991; Young, 1994). Combined with the fact that the atmosphere is probably pure N_2 having an atomic weight $\mu = 28$, the temperature of the atmosphere is 99.1 ± 8.1 K, or approximately 100 K. This value applies to the portions of the atmosphere above about 1–2 μb, where the occultation lightcurve is indicative of an essentially isothermal temperature structure (Elliot and Young, 1991).

A pure N_2 atmosphere at the low pressures indicated is non-absorbing both in the visible and in the infrared. Ignoring heat sources in the ionosphere, such an atmosphere should be approximately isothermal at the temperature of the surface, with perhaps a near-surface mixed layer where the temperature gradient is adiabatic. Estimates of Pluto's surface temperature vary significantly.

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The lowest values of these temperatures, $\simeq 35$ K (Stern *et al.*, 1993; Stansberry *et al.*, 1994; Quirico *et al.*, 1996a), typically refer to the temperature of the N_2 ice. Other estimates are higher, ranging from $\simeq 40$ K (Altenhoff *et al.*, 1988; Jewitt, 1994; Tryka *et al.*, 1994) up to 50–55 K (Sykes *et al.*, 1987; Tryka *et al.*, 1994; Stansberry *et al.*, 1994). All of these temperatures are considerably lower than the 100 K temperature of the upper atmosphere discussed above. This implies that there is a heat source in Pluto's atmosphere which operates to raise the temperature to 100 K. It is also certain evidence that there is a temperature gradient (inversion) below about 1 μb in Pluto's atmosphere, because a smooth transition must occur between the 100 K upper atmosphere and the much lower temperature of the surface. Such a temperature structure must be the dominant cause of the "knee" in the 1988 Pluto occultation lightcurve. This follows because the temperature inversion is now known to exist; a heat source with the correct characteristics has been proposed which explains such a structure (Yelle *et al.*, 1995; Lellouch, 1994; Strobel *et al.*, 1996); physically plausible temperature inversions would produce lightcurves such as were seen during the occultation (Hubbard *et al.*, 1990; Stansberry *et al.*, 1994; Strobel *et al.*, 1996); and no physically plausible haze layer could cause the "knee" (Stansberry *et al.*, 1989; Lellouch, 1994; Strobel *et al.*, 1996).

Yelle and Lunine (1989) demonstrated that CH_4 could provide a considerable heat source in Pluto's atmosphere. Their model has been revised to include cooling by CO and heating by aerosols (Lellouch, 1994), and that model has additionally been improved upon by Strobel *et al.* (1996), who do a more detailed calculation of the radiative transfer in the CH_4 bands responsible for the net heating. Yelle and Lunine concluded, before the discovery of N_2 in Pluto's spectrum, that if methane were present at mixing ratios greater than 0.001, the atmospheric temperature would be approximately 100 K. This finding turned the idea that Pluto's atmosphere was dominantly CH_4 on its head: the occultation value of T/μ could not be reconciled with this temperature and a molecular mass of only 16. However, subsequent to the finding that Pluto's surface was dominated by N_2, the difficulty has instead been to reconcile the high atmospheric temperature with the extremely low CH_4 mixing ratios expected from vapor pressure equilibrium with Pluto's surface ices, 3.7×10^{-6}, as opposed to the >0.001 that is required in the Yelle and Lunine methane heating model.

This problem has been exacerbated in the models of Lellouch (1994) and Strobel *et al.* (1996) by the inclusion of CO in the atmosphere. Lellouch selected a CO mixing ratio of 7.5×10^{-4}, 1.5 times larger than what we calculated above, by extrapolating from the composition of Triton's surface ices and atmosphere. Strobel *et al.*, use 4.6×10^{-4}, essentially the same as our value. Lellouch required a CH_4 mixing ratio $\geq 10\%$ in order to give an atmospheric temperature of 105 K, while Strobel *et al.*, need $\simeq 2\%$. Both focus on the inability of their models to produce steep temperature inversions (≥ 10 K km^{-1}) at around the 2 μb level. While this gradient was cited by Hubbard *et al.* (1990) as necessary to match the shape of the "knee" in the 1988 KAO occultation lightcurve, the drop in stellar flux in the occultation is actually related to the second derivative of temperature with altitude, not the temperature gradient. Stansberry *et al.* (1994) point this out in the context of their lightcurve models, which formally require $dT/dz \simeq 30$ K km^{-1}. The Hubbard *et al.* (1990) value, while derived from an inversion technique rather than a forward model, used a smooth fit to an early version of the KAO lightcurve as the basis for the inversion. In order to establish the temperature gradient in Pluto's lower atmosphere with any confidence, two things need to be done: (1) Detailed forward models using temperature profiles such as have been generated by Yelle and Lunine, Lellouch, and Strobel *et al.* should be done, and fit to the entire KAO data set (Stansberry *et al.* (1994) only fit to three fiducial points derived from the data set and used a somewhat arbitrary functional form). (2) The KAO data set should be inverted directly to derive the magnitude of the temperature inversion in the lower atmosphere. Until this happens the steepness of the temperature inversion should be regarded as uncertain, with the 10 K km^{-1} value quoted by Hubbard *et al.*, as the best estimate. The most important well-defined constraint on atmosphere models is that they produce atmospheric temperatures of 100 K above the 1–2 μb level, and that the atmosphere is isothermal over a few scale heights above that. A CH_4 mixing ratio greater than or equal to 1% seems to be required by the newer models just discussed.

Young (1994) has recently used high-resolution spectroscopy to examine the absorption lines formed by CH_4 in Pluto's atmosphere to directly measure the CH_4 abundance. It may be possible to extend this technique to directly measure the temperature of the CH_4 gas, but at this point it provides a measurement of the column abundance, $\xi = 1.2^{+3.2}_{-0.87}$ cm amagat. The column abundance can be converted into a mixing ratio, χ, given the surface pressure, P, and scale height of the atmosphere, H, through $\chi = N_0RT\xi/N_APH$, where N_0 is Loschmidt's number, R the gas constant, T the atmospheric temperature, and N_A is Avagadro's number. Taking $T = 100$ K we find that Young's upper bound on ξ gives $\chi \geq 1\%$ for surface pressures less than 33 μb, with the best fit ξ and $\chi = 1\%$ implying a surface pressure of 8.9 μb. Assuming the atmosphere is in vapor pressure equilibrium with N_2 ice, these pressures correspond to ice temperatures of 39 and 37 K, respectively, a few Kelvin lower than the results of Tryka *et al.* (1994). However, Young (1994) notes that improvements to the CH_4 rotational spectrum analysis will probably increase the estimate of the column abundance, so we nominally adopt the Tryka *et al.*, value of 40 K for the temperature of N_2 on Pluto's surface.

The foregoing considerations lead us to conclude that Pluto's atmosphere must have a CH_4 mixing ratio $\chi \geq 1\%$, both in order to satisfy the constraints of the KAO lightcurve subject to a predominantly N_2 atmospheric composition, and to satisfy the measurements of Young (1994). A 1% mixing ratio is a factor of $\simeq 2.7 \times 10^3$ larger than the mixing ratio we calculated above assuming that the CH_4 is in ideal solid solution with the N_2 ice. We argue below that patches of pure CH_4 ice cannot be in vapor pressure equilibrium at 40 K with CH_4 gas in Pluto's atmosphere. However, if they were, the mixing ratio would only be approximately 0.01%, a factor of 100 lower than what we require. Similar calculations below show that Triton's atmosphere is also enriched in CH_4 (by a factor of $\sim 10^3$) relative to the prediction one would make based on Raoult's law and using the N_2:CH_4 ratio discussed by Cruikshank *et al.* (1993).

In this paper we describe laboratory evidence for the segregation of CH_4 ice grains from a N_2:CH_4 solid solution as a result of sublimation. The sublimation of such deposits will be greatly influenced by the presence of the $\simeq 99\%$ N_2 atmosphere. We have modeled this interaction (both for CH_4 sublimation and condensation), using standard turbulent boundary layer theory, modified to include molecular diffusion in the lowest layers. This theory leads to two basic conclusions: (1) that CH_4 patches will have higher temperatures than the N_2:CH_4 solid solution which dominates the surface, and (2) that the contrast between the efficiency of sublimation and condensation of CH_4 leads to elevated atmospheric mixing ratios. The model can produce atmospheric CH_4 mixing ratios of 1% for a range of plausible assumptions about Pluto's atmosphere and surface, in accord with the compositional requirements discussed above. We briefly discuss the fact that Triton's atmosphere also has too much CH_4, and note how our model can explain those observations. Finally some of the seasonal implications of the model are explored.

Segregation of CH_4

Laboratory studies (Quirico and Schmitt, 1996; Quirico *et al.*, 1996a) indicate that the absorption features of CH_4 ice are measurably shifted in wavelength when the CH_4 is dissolved in N_2 ice. Initial analyses of Pluto's spectrum (Owen *et al.*, 1993; Quirico *et al.*, 1996b; Schmitt *et al.*, 1996) show that the CH_4 features are in fact shifted, consistent with a N_2 : CH_4 solid solution. However, the bands also indicate a second, unshifted component, indicative of either pure CH_4 ice, or ice in which CH_4 is highly concentrated (Cruikshank *et al.*, 1996; Quirico and Schmitt, 1996). This finding is backed up by the visible spectrum of Pluto (Grundy and Fink, 1996), which also shows the combination of shifted bands, due to CH_4 in solid solution with N_2, and unshifted bands due to pure CH_4 ice.

Fractional sublimation. The presence of some pure CH_4 ice on Pluto should not be a surprise. Lunine and Stevenson (1985) predicted that the two species would be segregated on Triton as a result of seasonal transport and the large volatility difference between the two. Trafton (1990) developed a globally averaged seasonal model which predicted a very thin (a few molecules thick) "detailed balancing" layer of nearly pure CH_4 overlying the N_2 : CH_4 solid solution (see also Spencer *et al.* (1996) and the following discussion). Quirico *et al.* (1996a) have also observed the formation of nearly pure CH_4 grains during condensation of dilute mixtures of CH_4 in N_2 gas onto a cold substrate.

A quantitative description of the compositional evolution of a sublimating layer of a solid solution composed of two species with different volatilities can be derived given an expression relating the composition of the solid to that of the gas which sublimates from it. Raoult's law provides just such a relationship. Taking the particular case of CH_4 dissolved in N_2 it states that the CH_4 mole fraction of the gas in equilibrium with the solid solution is given by

$$\chi = \frac{XP^{\mathrm{vp}}_{\mathrm{CH}_4}}{XP^{\mathrm{vp}}_{\mathrm{CH}_4}+(1-X)P^{\mathrm{vp}}_{\mathrm{N}_2}} \tag{1}$$

where $P^{\mathrm{vp}}_{\mathrm{CH}_4}$ and $P^{\mathrm{vp}}_{\mathrm{N}_2}$ are the saturation vapor pressures of CH_4 and N_2, and X is the mole fraction of CH_4 in the solid solution. The total sublimation flux of molecules will be a mixture of N_2 and CH_4, with the mole fraction of each in the gas specified by Raoult's law (assuming sublimation under near equilibrium conditions). The time derivative of X may be written as

$$\frac{\mathrm{d}X}{\mathrm{d}t} = \frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{n_{\mathrm{CH}_4}}{n}\right) = \frac{1}{n}\frac{\mathrm{d}n_{\mathrm{CH}_4}}{\mathrm{d}t} - \frac{n_{\mathrm{CH}_4}}{n^2}\frac{\mathrm{d}n}{\mathrm{d}t} = -\frac{\dot{n}}{n}(X-\chi) \tag{2}$$

where n_{CH_4} is the number of CH_4 molecules in the solid, and n the total number of molecules in the solid. In the last part of equation (2) time derivatives have been denoted with a dot, we have set $\dot{n}_{\mathrm{CH}_4} = \chi\dot{n}$, and we have ignored the different molar volumes of CH_4 and N_2 in the solid.

Given an initial inventory of molecules, equations (2) and (3) can be solved for the composition of the solid solution, X, as a function of time as it sublimates. There are two limiting cases to consider: the sublimation of a seasonal layer where the composition is always assumed to be homogeneous, and sublimation of a layer where the composition is equal to the initial composition below the topmost layer, while the composition of the topmost monolayer reflects all of the effects of the fractional sublimation. The first case is equivalent to assuming that solid-state diffusion is extremely efficient, while the second (much more realistic) case is equivalent to assuming that solid-state diffusion is nonexistent. In the second case, the topmost layer quickly becomes enriched in CH_4 as the ice sublimates. The volatility contrast between CH_4 and N_2 is so large, $\simeq 10^4$, that essentially none of the CH_4 sublimates. (The composition of the sublimating gas, χ, only reaches 0.5 for a solid composition $X = 0.9999$.) If the initial composition of the solid solution (assumed constant throughout the layer) is X_0, a monolayer of CH_4 molecules will form after approximately $(1/X_0)\ln(1/X_0)$ monolayers have sublimated from the surface. For $X_0 = 0.01$ the CH_4 monolayer will form after about 460 monolayers have sublimated. The typical net sublimation rate for Pluto is about $1\,\mathrm{g\,cm^{-2}\,yr^{-1}}$, or one monolayer per second. So for the case where solid state diffusion is neglected, the topmost layer of molecules of a sublimating layer of solid solution will be essentially pure CH_4 after 460 s of sublimation, or within about 8 min. Including estimated solid-state diffusion coefficients (Eluszkiewicz, 1991) in this calculation approximately doubles the amount of time required for the CH_4 monolayer to form (Spencer *et al.*, 1996).

The existence of the CH_4 monolayer was previously predicted by Trafton (1990). The difference between the model he proposes and this model lies in the effect the CH_4 coating has once it forms. In Trafton's model the "monolayer" is actually several molecules thick because it is dynamically maintained as individual molecules exchange with the gas—it is what he refers to as a "detailed balancing" layer. The composition of the layer is such that it is in equilibrium with a gas having the same composition as the underlying solid solution, i.e. $\chi = X_0$. For Pluto this implies $\chi \simeq 1\%$, approximately the atmospheric mixing ratio which seems to be required by models of Pluto's atmospheric temperature structure. A second prediction of that model is that the total pressure in equilibrium with the solid solution is greatly reduced by the presence of the detailed balancing layer. A particular model (see Spencer *et al.*, 1996) which gives $\chi = 1\%$ and a total surface pressure of 3 μb, equal to the deepest level probed in the KAO occultation lightcurve (Elliot and Young, 1992), requires a 42 K temperature for the solid solution. Without the detailed balancing layer the vapor pressure at that temperature would be 158 μb.

We propose an alternative to the detailed balancing layer, namely that as CH_4 builds up at the surface due to fractional sublimation, it forms a layer of relatively long-lasting grains. This grainy layer has little or no influence on sublimation from the underlying solid solution, at least until the layer of grains grows to be quite deep. This hypothesis seems to be qualitatively supported by our experiments on sublimating a sample of N_2:CH_4 solid solution.

Laboratory data. We have measured the transmission spectrum through a sample of sublimating N_2:CH_4 solid solution as a function of time in the regions of the 2.38 μm band of CH_4 and of the 2.15 μm band of N_2. Details on the laboratory setup at LGGE and on the thin film techniques used for this experiment are described elsewhere (Schmitt *et al.*, 1994; Quirico and Schmitt, 1996). The original sample was a dilute (0.2%) solution of CH_4 in N_2 ice approximately 1 mm thick and slowly condensed at 26 K on an infrared window. After condensation, the temperature of the sample was rapidly raised to 34 K and, after an initial spectrum was recorded, a new spectrum was taken typically every hour during sublimation of the sample. The sublimation of N_2 and the decrease of the sample thickness was monitored with the strength of the narrow 2.148 μm band of α-N_2 (Grundy *et al.*, 1993). The sublimation rate of N_2 was about 70 $\mu m\,h^{-1}$ (60 $cm\,yr^{-1}$) and complete sublimation took about 14 h. Sublimation of CH_4 and change of its physical state were quantitatively monitored through the $\nu_1 + \nu_4$ band near 2.38 μm. It was found that for pure CH_4 this band occurs at 2.379 μm, but that it is strongly shifted towards 2.371 μm when CH_4 is diluted in α-N_2 (Quirico and Schmitt, 1996; Quirico *et al.*, 1996a). The two peaks $\simeq 0.004$ μm wide, being separated by approximately 0.008 μm, and our spectral resolution being ~ 4000, we cleanly resolved the shape and location of the bands. Empirical band models were fit to the separate bands in order to determine their peak intensities.

Figure 1 shows a time series of measured spectra taken during the sublimation experiment. The initial spectrum (solid line with triangles) is dominated by the 2.371 μm peak characteristic of CH_4 diluted in α-N_2, with a small shoulder on its high wavelength side, probably due to a partial segregation of CH_4 during condensation of the sample (about 15% of the total CH_4). Whether this absorption is due to very small grains of pure CH_4 ice in the sample, or to isolated clusters of a few molecules is not clear. The difficulty in preparing a sample of the solid solution in which the CH_4 is perfectly dissolved in the N_2 is due to the very low solubility (2%) of CH_4 in α-N_2 at 26 K. As the sample sublimated the pure CH_4 peak at 2.379 μm grew, while the shifted peak at 2.371 μm decreased in strength. The final spectrum in Fig. 1 (solid line with circles) consists only of absorption by CH_4 in its pure form.

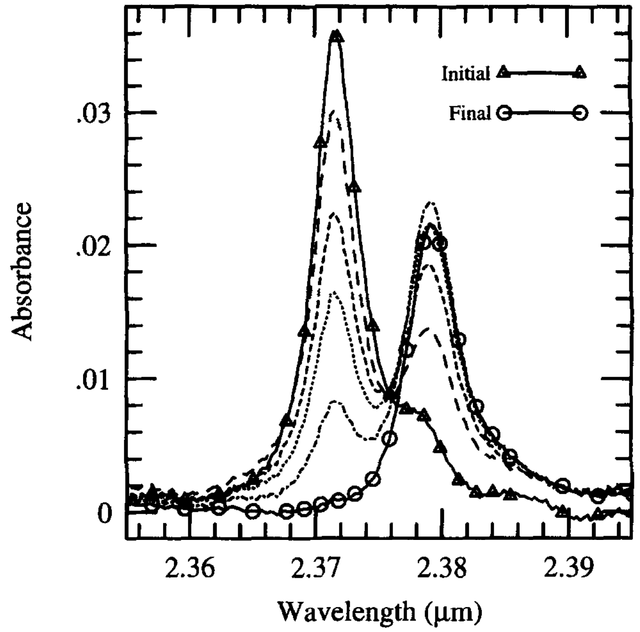

Fig. 1. Evolution of the 2.379/2.371 μm bands of CH_4 during the sublimation of a N_2:CH_4 solid solution (0.2% CH_4). The solid line with triangles is the initial spectrum measured before any sublimation had occurred; the solid line with circles is the final spectrum. The band at 2.371 μm corresponds to CH_4 in solid solution with N_2, while the 2.379 μm component is due to nearly-pure CH_4 appearing in the sample. Spectra shown were taken at 0, 2.75, 5, 7.75, 11 and 21.3 h from the beginning of the experiment

The peak absorbances of the pure and diluted CH_4 bands, as well as the thickness of the sample (N_2) as a function of time are plotted in Fig. 2. The absorption in the pure CH_4 band starts at a level greater than zero as explained above. As the sample sublimates, its thickness decreases roughly linearly with time, and the absorption in the pure CH_4 band increases approximately linearly as well, while the absorption in the diluted CH_4 band decreases linearly. As the experiment progresses the sample continues to sublimate at approximately the same rate, with a corresponding linear decrease in the absorption by CH_4 in solution, while the absorption in the pure CH_4 band increases more slowly than at first. At the end of 15 h a residue of CH_4 grains approximately 1 μm thick remained.

The simplest interpretation of these data is that a crust of CH_4 grains develops on top of the sublimating solid

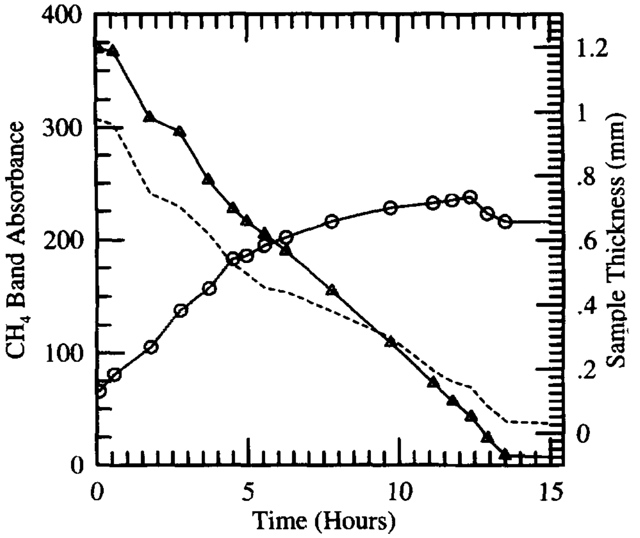

Fig. 2. The results of a laboratory experiment measuring the composition of a sample of N_2:CH_4 solid solution vs. time as it sublimated. The initial composition was 0.2% CH_4 and the sublimation temperature was 34 K. The dashed line is the thickness of the sample (right axis, mm) as a function of time as the sample sublimated. The solid line with triangles is the absorbance in the shifted (2.371 μm) CH_4 band formed by CH_4 in solid solution with the N_2, while the solid line with circles is the absorbance in the unshifted (2.379 μm) CH_4 band formed by pure or nearly-pure CH_4

solution in the experimental chamber while the composition of the underlying solid solution is not altered. We suspect that the accumulation of pure CH_4 slowed down about half-way through the experiment because they were only loosely bound to the surface once they formed. The free surface of the sample was vertical during the experiment, and we suspect that some of the grains simply fell out of the beam to the bottom of the cell.

The crust has little influence on the sublimation rate of the underlying solid solution as can be seen from the slope of the data for the sample thickness in Fig. 2. This behavior is qualitatively unlike what we would expect if a "detailed balancing" layer had formed during the experiment. First, a detailed balancing layer would greatly reduce the sublimation rate of the solid solution, and second, the pure CH_4 band would be extremely weak and would not change in strength, since the detailed balancing layer is never more than a few molecules thick. However, Trafton's detailed balancing layer is predicted to form under conditions near equilibrium (i.e. low sublimation rates), while this experiment was done with a sublimation rate approximately 60 times larger than is typical for Pluto. Likewise, the fact that a porous crust of CH_4 grains formed in the experiment cannot be taken as conclusive evidence that the same will happen during sublimation of solid solutions on Pluto, again, because of the disparity in sublimation rates. The applicability of the experiment is also somewhat in question because it was performed in the α-N_2 temperature regime rather than in the β-N_2 regime. We do not expect fundamental differences due to the phase of the N_2 ice except a slight delay in the formation of the CH_4 layer, as described next. We hope to rectify these shortcomings in future experiments, but for the time being do hold that this experiment is at least suggestive that fractional sublimation will lead to the formation of a grainy CH_4 layer rather than a detailed balancing layer.

The observation that CH_4 formed a discontinuous, grainy layer over the N_2-rich solid solution is consistent with the N_2:CH_4 solid phase diagram. Prokhvatilov and Yantsevich (1983) find that β-N_2 can only accommodate about a 5% mole fraction of CH_4 within its structure at 40 K. For solids with larger mole fractions of CH_4 the structure consists of grains of β-N_2 saturated with CH_4 mixed with a few grains of β-CH_4, which in turn contain about 5% N_2. The implications of this for the fractional sublimation scenario are that as the topmost layer reaches a CH_4 concentration of about 5% it will become saturated, and further concentration of CH_4 will, subject to kinetics, tend to form grains of β-CH_4, rather that simply increasing the concentration of the CH_4 in solid solution with the N_2. This process will occur slightly earlier during the sublimation of α-N_2 with CH_4 dissolved in it, because α-N_2 becomes saturated with CH_4 at a mole fraction of only 2%. These grains of β-CH_4 will be mechanically separate from the β-N_2 (or α-N_2) grains at the microscopic level, offering a natural explanation for the observations described above.

Application to Pluto. The experimental data and reasoning presented above lead us to conclude that it is plausible that areas of sublimating N_2:CH_4 ice on Pluto (and presumably Triton) will eventually wind up with a layer of nearly pure CH_4 grains at their upper surfaces. Continuing sublimation, primarily from the underlying solid solution, will result in an ever increasing depth for the lag deposit of CH_4 grains. During this stage we hypothesize that N_2 sublimating from below and passing through the CH_4 lag deposit will control the temperature of the CH_4. Eventually the layer may either be thick enough to choke off sublimation of the solid solution, the CH_4 grains may anneal into an impermeable layer, or the seasonal deposit of solid solution will entirely sublimate, leaving behind the layer of CH_4 grains. In either case, at this stage the residue of CH_4 grains becomes decoupled from the energetics of the predominantly N_2 ice. The temperature at which insolation, reradiation, and latent heat transport comes into balance for these CH_4 patches is higher than the temperature of the N_2 dominated ice. This is because CH_4 ice, while ostensibly a highly volatile substance, is much less so when it is sublimating into a dominantly N_2 atmosphere. This fact, which we demonstrate below, is critical for understanding the strong influence of CH_4 patches on Pluto's atmospheric composition.

Sublimation and temperature

Leighton and Murray (1966) showed that CO_2 ice on Mars would all have one temperature, regardless of where it was located, because of latent heat transport. It has been demonstrated that the same holds for either N_2 or CH_4 ice on Triton and Pluto (Trafton, 1984; Spencer, 1990; Stansberry, 1994; Spencer *et al.*, 1996). However, an exploration of the coupled transport of CH_4 and N_2

reveals that this isothermal volatile-ice paradigm does not apply to CH_4 patches if they develop on Pluto or Triton.

Single volatile case. Either N_2 or CH_4 ice on Pluto overlain by an atmosphere of the pure gas will be approximately isothermal because of the large latent heat of sublimation for either species and because the atmosphere is thick enough to be hydrostatic (Trafton and Stern, 1983; Trafton, 1984). This can be seen by comparing the sublimation latent heat flux to the flux of thermal radiation emitted by the surface. From kinetic theory the sublimation latent heat flux is just

$$L\dot{m} = L(P^{\mathrm{vp}}-P)\sqrt{\frac{\mu}{3RT}} \simeq L\left(\frac{P^{\mathrm{vp}}-P}{c_{\mathrm{s}}}\right) \tag{3}$$

where L is the latent heat of sublimation ($L_{N_2} = 2.5\times10^9\,\mathrm{erg\,g^{-1}}$; $L_{CH_4} = 5.5\times10^9\,\mathrm{erg\,g^{-1}}$), $\dot{m}$ the sublimation mass flux, P^{vp} the saturation vapor pressure, P the gas pressure, R the gas constant, T the temperature, c_{s} the sound speed, and a sticking coefficient of one has been assumed. Forming the ratio of this energy flux to the thermal flux gives a rough measure of the isothermality of the volatile ices:

$$I = \frac{L\dot{m}}{\sigma_{\mathrm{B}}T^4} = \left(\frac{L}{\sigma_{\mathrm{B}}T^4}\right)\left(\frac{P^{\mathrm{vp}}-P}{c_{\mathrm{s}}}\right) = \frac{L\Pi P}{c_{\mathrm{s}}\sigma_{\mathrm{B}}T^4}. \tag{4}$$

Here σ_{B} is the Stefan–Boltzmann constant, and $\Pi = (P^{\mathrm{vp}}-P)/P$ is the fractional pressure difference between the saturation vapor pressure and the atmospheric pressure. The volatile ices will be isothermal if the pressure difference required to drive the sublimation mass flux is small compared with the background pressure. Setting $\Pi = 0.1$ to account for this, taking $T = 40$ K, and using the vapor pressures of pure CH_4 and N_2 for P we find $I_{CH_4} = 1.2$ and $I_{N_2} = 5200$. To first order the temperature of N_2 ice on Pluto will be independent of the amount of insolation it receives. The temperature of CH_4 ice, if Pluto's atmosphere were pure CH_4, would depend somewhat on insolation, but latent heat transport would be roughly equally important for determining the temperature. However, Pluto's atmosphere is dominantly nitrogen, and this vastly reduces the sublimation energy flux for CH_4.

CH_4 *Sublimation into* N_2. A molecule sublimating from a CH_4 patch on Pluto or Triton will generally collide not with one of its siblings, but with a N_2 molecule. This will inhibit the ability of CH_4 molecules to rapidly escape from the surface, effectively limiting the CH_4 sublimation flux to that which can diffuse or be turbulently mixed into the N_2 atmosphere. We adopt the semi-empirical Monin–Obukhov similarity (M.O.) theory for forced convection, developed from extensive studies of atmospheric heating and the evaporation of H_2O on Earth (cf. Arya, 1988), to model the sublimation of CH_4 into Pluto's atmosphere. This theory has previously been applied to heating of Mars' atmosphere (Sutton *et al.*, 1978), Triton's atmosphere (Stansberry *et al.*, 1992), and Pluto's atmosphere (Stansberry *et al.*, 1994). M.O. theory has also been applied to the sublimation of H_2O on Mars by, e.g. Blumsack *et al.* (1973), and Flasar and Goody (1976). This approach embodies the effects of winds, the buoyancy of the CH_4 in the N_2, as well as the influence of a thin, near-surface layer where molecular diffusion plays an important role.

Here we follow the development given in Stansberry *et al.* (1992) for atmospheric heating on Triton, outlining the minor changes necessary for computing mass fluxes of CH_4 rather than heat fluxes. The depth of the layer where wind-shear induced turbulence dominates over buoyancy is given by the Monin–Obukhov length

$$\mathcal{L} = \frac{u_*^3}{k_{\mathrm{v}}}\frac{T_{\mathrm{v}}}{g}\frac{\rho}{0.75\dot{m}}. \tag{5}$$

Here u_* is the friction velocity, $k_{\mathrm{v}} = 0.4$ is Von Karman's constant, $T_{\mathrm{v}} = T[1+0.75\chi]$ the virtual temperature, g the acceleration of gravity, ρ the average atmospheric density in the boundary layer, and χ the CH_4 mixing ratio. The value 0.75 in equation (5) and T_{v} is given by $(\mu_0/\mu)-1$, where $\mu_0 = 28$ is the molecular mass of the atmosphere, and $\mu = 16$ the molecular weight of CH_4. The use of T_{v} in equation (5) accounts for the buoyancy of the CH_4 gas. $\mathcal{L}$ is the length scale for defining the gradient in atmospheric composition: when $\mathcal{L}$ is small, the compositional gradient is large and the flux of CH_4 is also large. $\mathcal{L}$, as a measure of the thickness of the layer where turbulence dominates buoyancy, also depends on the strength of the winds: for higher winds $\mathcal{L}$ is larger. Typical values we find for $\mathcal{L}$ are on the order of 200 m in areas where CH_4 is sublimating, and on the order of 10 km in areas where it is condensing from the atmosphere. The sign of $\mathcal{L}$ reflects the stability of the atmospheric virtual temperature profile, i.e. it is unstable for sublimation of CH_4 from the surface, and stable for condensation of CH_4 from the atmosphere.

The second scale factor required by the M.O. theory normalizes the mixing ratio of CH_4 and is given by

$$\chi_* = \frac{\dot{m}}{\rho u_*} \tag{6}$$

where ρ is the atmospheric density. In terms of χ_* and $\mathcal{L}$, the mole fraction of CH_4 as a function of height above a source or sink is then found from

$$\frac{\mathrm{d}\chi}{\mathrm{d}z} = \frac{\chi_*}{k_{\mathrm{v}}z}\Phi(z/L) \tag{7}$$

where z is height, and $\Phi(z/\mathcal{L})$ an empirically determined function of height and the Monin–Obukhov length (Businger *et al.*, 1971). Integrating equation (7) provides an expression for the mass flux as a function of the change in CH_4 concentration between the surface and the height of interest:

$$\dot{m} = -\rho u_* C_{\mathrm{m}}(\chi|_z - \chi|_{z=0}) = -\rho u_* C_{\mathrm{m}}\Delta\chi. \tag{8}$$

C_{m} is the mass transfer coefficient, and contains all of the physics of the diffusive and turbulent mixing of CH_4 into the atmosphere. Sutton *et al.* (1978) found that at low densities molecular diffusion is the dominant interaction process near the surface. Below we calculate the depth of the molecular diffusion sublayer, z_* in Pluto's atmosphere; here we define C_{m} such that it includes the effects of that sublayer:

$$C_{\mathrm{m}} = k_{\mathrm{v}}\left[1+\int_{z*}^{z}\frac{1}{z'}\Phi(z'/L)\,\mathrm{d}z'\right]^{-1}. \tag{9}$$

$\Phi(z/\mathscr{L})$ has two forms depending on the sign of $\mathscr{L}$, and therefore on whether we are considering sublimation or condensation (cf. Sutton *et al.* (1978) or Stansberry *et al.* (1992)). In our calculations we integrate from z_* to a height of 2 km. Integrating to higher altitudes produced no change in our computed values for C_{m} or the mass fluxes. Next we estimate the thickness of the near-surface molecular-diffusion sublayer, z_*.

The depth of the surface layer where molecular diffusion dominates over turbulence is given by $z_* = \kappa/k_{\mathrm{v}}u_*$, where κ is the molecular diffusion coefficient. The friction velocity on Pluto is unknown. Ingersoll and Tryka (1990) estimated that on Triton $u_* = 24\,\mathrm{cm\,s^{-1}}$, but sublimation driven winds on Pluto are likely to be weaker than on Triton. The subsolar latitude on Triton was $-45°$ at the time of the Voyager encounter, resulting in very high insolation on the N_2 ice South Polar Cap. The resulting rather strong sublimation-driven flow (wind speed of $10\,\mathrm{m\,s^{-1}}$ (Ingersoll, 1990)), along with considerations of the Corriolis force and surface stress, led them to the above value for u_*.

On Pluto the subsolar point is currently near the equator, and it was even closer in 1989 when the stellar occultation was observed. If Pluto's volatiles are mostly confined to polar caps, as seems to be indicated by the albedo maps (Buie *et al.*, 1992; Young and Binzel, 1994; Drish *et al.*, 1995), very little interhemispheric flow will occur: the predominant transport will be from the edges of the caps towards the poles. If the caps are disparate in size some interhemispheric transport can occur. Wind speeds in that case can be estimated by separately calculating the energy balance for each cap while requiring their temperatures to be the same. Doing so, we find that the maximum sublimation driven interhemispheric wind speed is approximately $1\,\mathrm{m\,s^{-1}}$. The corresponding friction velocity would be $u_* = 2.4\,\mathrm{cm\,s^{-1}}$, assuming the same drag characteristics for Pluto's surface as Ingersoll and Tryka assumed for Triton. Stansberry *et al.* (1994) have shown that atmospheric heating by Pluto's surface is an order of magnitude stronger than it is on Triton. Winds driven by heating could well dominate lower atmospheric flow, but it is difficult to estimate their speed. In order to allow for these uncertainties we use $u_* = 6$, 12, and $24\,\mathrm{cm\,s^{-1}}$ in the calculations below, but in the interest of brevity will only discuss the results for $u_* = 12\,\mathrm{cm\,s^{-1}}$ (corresponding to a wind speed of approximately $5\,\mathrm{m\,s^{-1}}$) unless otherwise noted. The binary gas diffusion coefficient of CH_4 in N_2 at 40 K and 58 μb is $230\,\mathrm{cm^2\,s^{-1}}$ (Reid *et al.*, 1977). Taking the above values for u_*, this means the depth of the sublayer where CH_4 transport is dominated by molecular diffusion is in the range 7–27 cm, with our nominal value being 14 cm.

Above this diffusive sublayer, CH_4 transport is dominated by eddy diffusion. The depth of the layer where eddies are important is given by the magnitude of $\mathscr{L}$ (our calculated values range from a few hundred meters in areas where CH_4 is vigorously sublimating, to a few kilometers in areas where CH_4 is condensing at the surface). In this layer (the planetary boundary layer, or PBL), sheer stresses induced by the interaction of the wind with the surface result in sheer in the wind velocity field, which produces eddies. Above the PBL vertical CH_4 transport is dominated by the buoyancy of the CH_4 in the N_2 atmosphere. We will later assume that above the PBL the composition of the atmosphere is laterally homogeneous, i.e. that CH_4 gas sublimating from patches is efficiently mixed in the PBL such that the composition of the atmosphere higher up is everywhere the same. The physics of the diffusive and turbulent transport of CH_4 through the PBL and the diffusive sublayer is embodied in u_* and C_{m}.

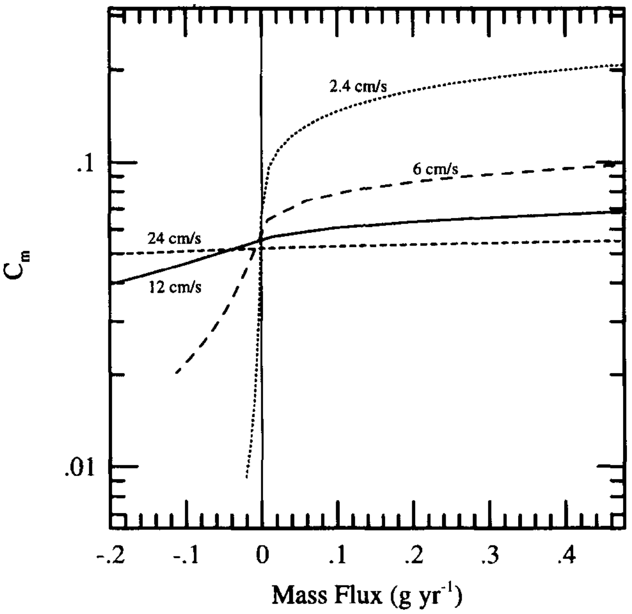

Fig. 3. The vertical mass transport coefficient for CH_4 in Pluto's atmosphere vs. the CH_4 mass flux at the surface. The vertical line divides the sublimation regime (mass fluxes >0) from the condensation regime. Each curve was calculated for a different friction velocity, shown by the labels

Figure 3 illustrates the dependence of C_{m} on u_* and the mass flux of CH_4 sublimating from (positive fluxes) the surface or condensing onto (negative fluxes) the surface. The strong dependence of C_{m} on the sign of the mass flux reflects the importance of methane's buoyancy in the N_2 atmosphere. At smaller wind speeds, corresponding to smaller friction velocities, buoyancy is increasingly the dominant factor. If Pluto's winds are only $1\,\mathrm{m\,s^{-1}}$ ($u_* = 2.4\,\mathrm{cm\,s^{-1}}$), the contrast between C_{m} for getting CH_4 into the atmosphere vs. transporting it to the surface is over an order of magnitude. On the other hand, if Pluto's winds are as strong as Triton's ($u_* = 24\,\mathrm{cm\,s^{-1}}$) there is almost no contrast between the efficiency of upward and downward mass transport. (Note, however, that this does not imply that the magnitude of the upward and downward fluxes will be equal on Triton. The dependence of $\Delta\chi$ in equation (8) will still lead to a large contrast between them.)

Figure 4 shows the absolute magnitude of the CH_4 mass fluxes we compute vs. the temperature of CH_4 ice on the surface for a variety of conditions. The computations are for an assumed 58 μb of N_2 in equilibrium with its ice on the surface at 40 K, consistent with the results of Tryka *et al.* (1994). Panels a, b, and c, are for CH_4 mixing ratios $\chi = 5$, 1, and 0.2%. Each panel shows the fluxes for fric-

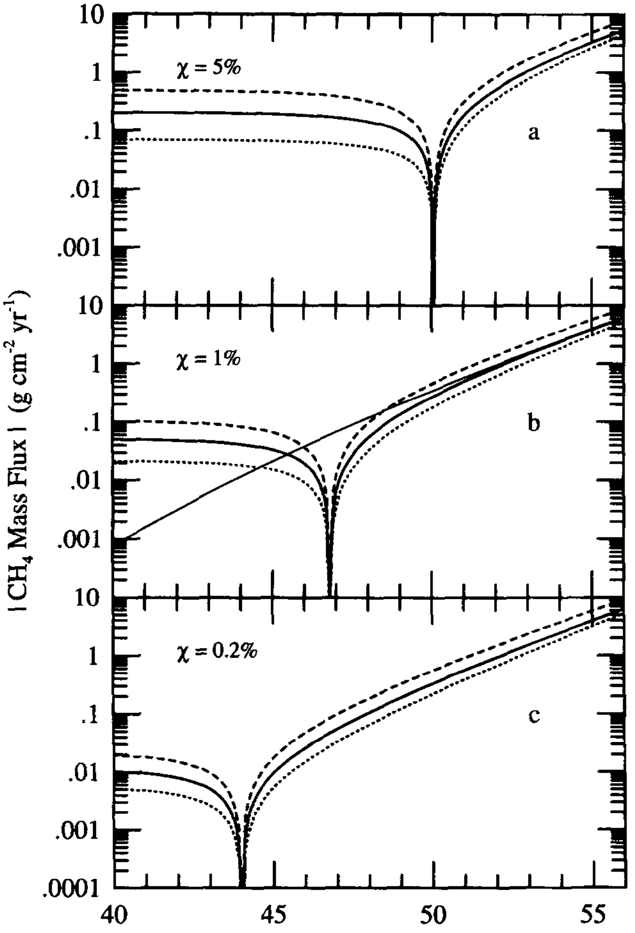

Fig. 4. The magnitudes of CH_4 sublimation (upward) and condensation (downward) mass fluxes calculated according to Monin–Obukhov theory as a function of the temperature of CH_4 patches on the surface. In all three panels the dashed, solid and dotted lines are for $u_* = 24$, 12, and $6\,\mathrm{cm\,s^{-1}}$, respectively. The atmospheric composition $\chi = 5$, 1, and 0.2% in panels a, b, and c, respectively. Each panel shows a minimum at the equilibration temperature, T_q, where the partial pressure of CH_4 in the atmosphere equals the vapor pressure of the CH_4 ice. Upward (sublimation) fluxes are to the right of the minima, downward (condensation) fluxes to the left. The nearly straight, thin solid line in panel b is the maximum upward mass flux calculated by setting $\chi = 0$. The total surface pressure is 58 μb, corresponding to a N_2 ice temperature of 40 K

tion velocities $u_* = 6$, 12, and $24\,\mathrm{cm\,s^{-1}}$. The fluxes have a sharp minimum at the equilibration temperature, T_q, where the vapor pressure of the CH_4 ice is equal to the prescribed partial pressure of CH_4 in the atmosphere.

CH_4 patches with temperatures higher than T_q will supply CH_4 to the atmosphere, while all areas which are cooler can potentially act as sinks for CH_4. Thus condensation mass fluxes are to the left of T_q, and sublimation mass fluxes are to the right. Higher winds produce larger sublimation rates, as expected. The buoyancy of CH_4 in the dominantly N_2 atmosphere causes the contrast in magnitude between upward and downward fluxes. However, both the sublimation and condensation rates, 0.05 and $6.2\,\mathrm{g\,cm^{-2}\,yr^{-1}}$ at 40 and 55 K (for $u_* = 12\,\mathrm{cm\,s^{-1}}$), are much lower than would be computed from equation (3), which yields $1\,\mathrm{g\,cm^{-2}\,yr^{-1}}$ at 40 K, and $2700\,\mathrm{g\,cm^{-2}\,yr^{-1}}$ at 55 K (for $\Pi = 0.1$).

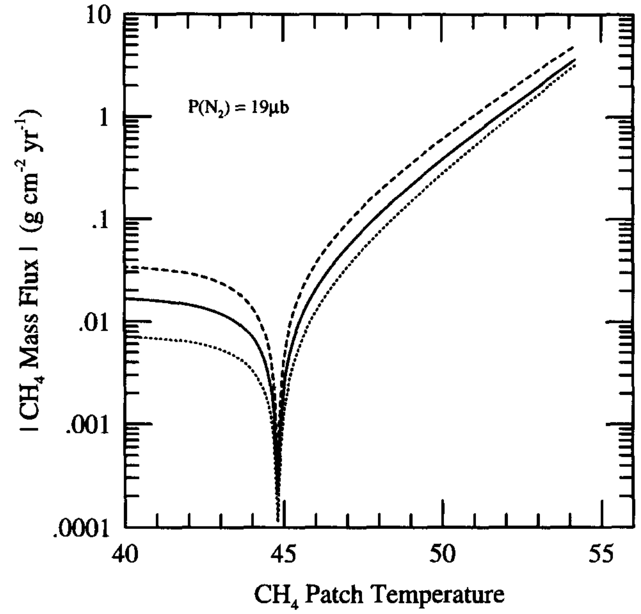

Fig. 5. Condensation and sublimation mass fluxes, as in Fig. 3, for a CH_4 mixing ratio of 1% and a total pressure of 19 μb, corresponding to a N_2 ice temperature of 38 K

A few degrees below T_q downward (condensation) rates asymptotically approach a temperature-independent value which is a function of the assumed mixing ratio: 0.2, 0.05, and $0.01\,\mathrm{g\,cm^{-2}\,yr^{-1}}$ for $\chi = 5$, 1, and 0.2%, respectively. This is because more than a few Kelvin below T_q, χ is essentially zero right at the surface, so in equation (8) $\Delta\chi$ is nearly equal to χ. A few degrees above T_q the logarithm of the upward (sublimation) rates tends towards an approximately linear increase with the temperature of the sublimating CH_4 patch. The thin solid line extending from the lower left corner in Fig. 4b to the upper right corner is the sublimation rate for $u_* = 12\,\mathrm{cm\,s^{-1}}$ if χ is set equal to zero. This is the maximum upward rate, and it can be seen that it defines the slope and magnitude of the sublimation flux in the limit that the patch temperature is greater that T_q by more than about 5 K. Since C_m is nearly independent of the sublimation mass flux for large values of the mass flux (Fig. 3), for patch temperatures this high the slope is just set by the slope of the vapor pressure curve of CH_4, as can be readily verified from this figure. It should also be noted that a comparison of panels a, b, and c of Fig. 4 show that the magnitude of the upward mass flux is only weakly dependent on χ at these temperatures, as long as χ is $\leq 10\%$.

Figure 5 shows our calculated CH_4 sublimation rates for a lower total surface pressure: the temperature of the N_2 ice is assumed to be 38 K, with a resulting vapor pressure of 19 μb. Only the results for $\chi = 1\%$ are shown. The major effects are to shift the equilibration temperature downward from, 46.9 K in Fig. 4 to 44.8 K, to reduce the asymptotic downward flux by a factor of 2.5, and to very slightly weaken the dependence of the upward rates on the CH_4 patch temperature. This happens because of the smaller density contrast, and resultant buoyancy force, between the sublimating CH_4 and the background N_2

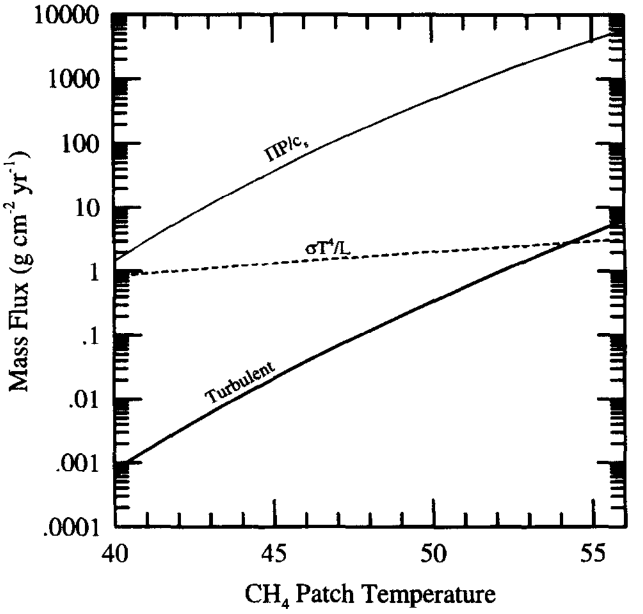

Fig. 6. CH_4 sublimation mass fluxes computed in three different ways vs. the temperature of a CH_4 ice patch on the surface. The kinetically limited mass flux (equation (3) with $\Pi = 0.1$ for CH_4 ice sublimating into CH_4 gas) is given as the thin solid line. The energy limited mass flux is given by the dashed line. The thick solid line gives our maximum ($\chi = 0$) upward CH_4 mass flux for turbulent diffusion through the lowest 2 km of the atmosphere

atmosphere when the N_2 pressure is lower. Again we find that these fluxes, 0.02 and 3.6 g cm^{-2} yr^{-1} at 40 and 55 K, respectively, are factors of 50 and 750 times smaller than those computed from equation (3).

Methane patch temperature. The greatly reduced CH_4 mass fluxes just illustrated have an important consequence for the temperature of CH_4 patches on the surface of Pluto. Using equations (3) and (4) we earlier demonstrated that the energy balance of CH_4 ice, if it were sublimating into a CH_4 atmosphere, would be about equally influenced by latent heat transport and thermal emission. However, the maximum (upward) sublimation rate shown in Fig. 4b is at least three orders of magnitude smaller than that predicted by equation (3) at all temperatures, so latent heat transport will be 1000 times less important for determining the temperature of CH_4 patches sublimating into a N_2 atmosphere. Figure 6 compares the CH_4 sublimation fluxes computed from equations (3) and (8) with the mass flux which would just balance thermal emission $\dot{m} = \sigma T^4/L$. This shows that on Pluto CH_4 sublimation into the N_2 atmosphere only becomes comparable to thermal emission at approximately 54 K. More than a few Kelvin below 54 K sublimating CH_4 patches will behave as if they are involatile in terms of their energy balance. Now we wish to know what temperatures to expect for them based on this conclusion.

Instantaneous equilibrium midday patch temperatures, assuming a bolometric albedo of 0.8 and emissivity of 0.9, will be 49 K. However, Trafton and Stern (1983) suggested that CH_4 may have a low emissivity in the far-IR, and this has been borne out by recent calculations (Stansberry *et al.*, 1996). Taking 0.8 for the emissivity of CH_4, midday patch temperatures will be 51 K, and 54 K for an emissivity of 0.6. Referring to Fig. 4b, where $\chi = 1\%$, at 51 K the upward flux is a factor of 10 larger than the largest downward flux, and in Fig. 5, for $\chi = 1\%$ and a total pressure of 19 μb, the upward flux exceeds the downward by an order of magnitude at 49 K. We will show below that "hot" CH_4 patches, i.e. those with temperatures several degrees above T_q, are capable of maintaining large mole fractions of CH_4 in Pluto's atmosphere.

Methane patch model

Above we have shown that seasonal sublimation of a N_2:CH_4 solid solution will likely result in areas dominated by CH_4 because of its comparatively low volatility compared to N_2. Our calculations of the rate of sublimation of such patches, and the rate at which CH_4 will condense on the surface from the atmosphere reveal that (1) CH_4 sublimates much more slowly when the effect of the N_2 atmosphere is taken into account, and that (2) sublimation is more efficient than condensation due to the buoyancy of the CH_4 gas in the dominantly N_2 atmosphere. The first point leads us to conclude that "hot" CH_4 patches will have temperatures well above the temperature of the N_2:CH_4 solid solution, and that during the daytime those temperatures can reasonably exceed the equilibration temperature with the CH_4 in the atmosphere by several degrees.

Because of the disparity in the CH_4 sublimation and condensation fluxes in Figs 4 and 5, CH_4 patches on Pluto will tend to increase the atmospheric mole fraction of CH_4 beyond what it would be in either the case of equilibrium with the N_2:CH_4 solid solution or in the case of simultaneous equilibrium over pure N_2 and CH_4 ices. We can estimate the atmospheric composition using a simple steady-state model for the amount of CH_4 sublimating and condensing from the atmosphere integrated over Pluto's entire surface. Equating the globally integrated rate CH_4 is added to the atmosphere by sublimation from patches to the globally integrated rate condensation removes it from the atmosphere gives

$$\dot{m}_{\rm up} A_{\rm patches} = \dot{m}_{\rm down} A_{\rm down}. \qquad (9a)$$

Here A represents the fraction of Pluto's surface, and the subscripts refer to sublimating (patches) and condensing (down) regions. This can be re-arranged to give the ratio $A_{\rm patches}/A_{\rm down}$, i.e. the ratio of the surface area covered by CH_4 patches to the surface area with temperatures less than T_q.

In order to estimate the fractional coverage of patches we need to know $\dot{m}_{\rm down}/\dot{m}_{\rm up}$. The downward fluxes are likely to be dominated by condensation onto N_2:CH_4 solid solution at 40 K. In these areas χ will be nearly zero at the surface, $\Delta\chi$ in equation (8) will be a maximum, and the downward flux will also be a maximum. Examining Fig. 4b this implies a downward CH_4 mass flux of 0.05 g cm^{-2} yr^{-1} for $u_* = 12$ cm s^{-1}. However, the upward fluxes are a strongly increasing function of temperature, and we have no specific knowledge of what the temperature of CH_4 patches on Pluto is. As a working model

Table 1.

Model parameter	Model 1[a]	Model 2[b]
Surface pressure (μb)	58	19
N_2 ice temperature (K)	40	38
CH_4 partial pressure (μb)	0.58	0.19
Equilibration temp., T_q (K)	46.8	44.8
Hot-patch temperature (K)	54	53
$\dot{m}_{up}/\dot{m}_{down}$	36	96
Fractional coverage of hot CH_4 patches (%)[a]	3	1

[a] $u_* = 12\,\mathrm{cm\,s^{-1}}$, $\chi = 1\%$ CH_4 in both models.
[b] Relative to all areas where $T < T_q$.

we adopt an instantaneous equilibrium temperature distribution for the patches. Under this assumption patch temperatures will vary as

$$T_{patch} = T_{ss}(1-(\cos\theta_{ss})^{1/4}) \tag{10}$$

where T_{ss} ($= 55$ K) is the subsolar point temperature and θ_{ss} the angular distance to the subsolar point. We also need an estimate of the fraction of the total area of CH_4 patches that is occupied by patches of a given temperature, $\delta A(T)$. A conservative approach is to assume that $\delta A(T) = \cos\theta_{ss}(T)\,\partial\theta_{ss}/\partial T\delta T$. Here $\theta_{ss}(T)$ is the solution of equation (10) for θ_{ss}, and δT a small increment of temperature. This is equivalent to assuming that CH_4 patches are evenly distributed across the surface, i.e. that they do not cluster near the subsolar latitude. As a result, this distribution underestimates the proportion of patches with high temperatures, and represents a conservative approach in that it will also underestimate the contribution of the hottest, most rapidly sublimating patches.

Using the above temperature distribution we calculated the area-weighted average sublimation mass flux of CH_4 for an atmospheric composition of $\chi = 1\%$ and found a value of $1.75\,\mathrm{g\,cm^{-2}\,yr^{-1}}$. From Fig. 4b this is the mass flux from a CH_4 patch at 53.5 K. From the same figure the downward CH_4 mass flux (for $u_* = 12\,\mathrm{cm\,s^{-1}}$) will be $0.05\,\mathrm{g\,cm^{-2}\,yr^{-1}}$. Using these mass fluxes and equation (9) to find $A_{patches}/A_{down}$ we find that if approximately 3% of Pluto's surface is covered with CH_4 patches the atmospheric composition will be 1% CH_4. If Pluto's surface pressure is 19 μb, rather than 58 μb as we have assumed above, we can use Fig. 5 to estimate that the downward mass flux is decreased from 0.05 to $0.02\,\mathrm{g\,cm^{-2}\,yr^{-1}}$, so that a 1% atmospheric mixing ratio can be maintained if 1% of Pluto's surface is covered by CH_4 patches.

Summary and conclusions

Table 1 summarizes two sets of parameters which will, according to the model we have just described, result in the mixing ratio of CH_4 in Pluto's atmosphere being 1%. The basic elements and assumptions underlying the model are further discussed below:

1. CH_4 patches form as a result of natural seasonal transport processes operating on Pluto. A patch consists of a region of nearly pure CH_4 ice grains on the surface, which is either thick enough to suppress the sublimation of the underlying N_2:CH_4 solid solution, or which overlies a non-volatile substrate. Before a developing layer of CH_4 grains reaches this stage, N_2 sublimation from below will effectively refrigerate the CH_4, even though the CH_4 itself is hardly sublimating. This hypothesis implies a subsidiary assumption that the detailed-balancing layer proposed by Trafton (1990) does not control the vapor pressure of Pluto's N_2:CH_4 solid solution. Although our initial experiments support this assumption, further experiments done at smaller sublimation rates will be required to resolve this issue. The nature of the N_2:CH_4 phase diagram suggests to us that the formation of nearly pure CH_4 grains on the surface of sublimating solid solutions is the typical outcome, rather than a detailed-balancing layer.
2. CH_4 patches, once formed, attain daytime temperatures ≥ 5 K higher than the CH_4 vapor equilibration temperature, T_q. This condition produces the contrast between the CH_4 sublimation and condensation fluxes, and therefore is critical for elevating the atmospheric mixing ratio. The condition is satisfied if CH_4 patches have an albedo of 0.8, and a far-IR bolometric emissivity $0.65 < \epsilon < 0.8$. According to the calculations of Stansberry *et al.* (1996) granular CH_4 ice will have emissivities in this range for grain sizes of about 1 mm. T_q depends on the total pressure, as can be seen by comparing Figs 4b and 5. Because of this, our model works best for lower surface pressures/N_2 ice temperatures. If Pluto's surface pressure exceeds 300 μb ($T_{N_2} > 43.4$ K), T_q is probably too close to the expected daytime high temperature for the model to operate. Likewise, CH_4 mixing ratios greater than 1% imply higher T_q values. For a surface pressure of 58 μb the model cannot produce a mixing ratio greater than about 5% unless CH_4 patches occupy a large fraction (> 10%) of the surface.
3. CH_4 does not condense in Pluto's lower atmosphere. If the CH_4 gas pumped into the atmosphere by patches condenses below a radius of 1250 km it cannot provide the high-altitude heating required to satisfy the occultation lightcurves. To zeroth order CH_4 would be expected to condense if the atmospheric temperature dropped below T_q. However, the atmospheric heating models of Stansberry *et al.* (1994) indicate that Pluto's lower atmosphere has a temperature of approximately 50 K, which exceeds or equals T_q for all of the cases explored in this study, so CH_4 is not expected to condense in the lower atmosphere. A separate issue is whether the CH_4 gas can efficiently mix into the upper atmosphere. The temperature inversion which lies somewhere between the surface and about 1205 km (Stansberry *et al.*, 1994) will strongly damp any turbulent motions, and might slow the mixing of CH_4 into the upper atmosphere where it is required.
4. We have ignored the effects of CO in both the surface ices and in the atmosphere. Since CO is marginally less volatile than N_2 it could potentially form "CO patches". There are no measurements directly con-

straining the mixing ratio of CO in Pluto's atmosphere as yet. If it is detected at enhanced levels it will be difficult to explain with this model because CO has the same molecular weight as N_2, and so will not have the same dynamics as CH_4.

5. We have ignored co-condensation of N_2. In the coldest areas where CH_4 is condensing on the surface N_2 will also be prone to condensing. We have assumed that the condensed solid has a composition determined from Raoult's law and the atmospheric composition. For $\chi = 0.01$ the solid will be almost pure CH_4. This implies that CH_4 gas has a net downward motion relative to the N_2 gas in the atmosphere in areas where it is condensing. If the atmosphere is freezing very quickly at the surface, the solid formed will have the same composition as the gas from which it was made, i.e. the composition will be quenched. If this happens on a large scale, downward mass fluxes of CH_4 will be different than we have calculated. However, we note that if condensation is happening in such a way that the atmospheric composition is quenched, this will lead to a downward CH_4 mass flux of about 0.01 g cm^{-2} yr^{-1} for $\chi = 1\%$. This downward flux is actually smaller than what we derive (Fig. 4b), so the ability of CH_4 patches to increase χ will be enhanced in this particular scenario. If instead we use the calculations for a total pressure of 19 μb (Fig. 5) there will be almost no effect on the model. We also note that because the CH_4 is present at a vapor pressure with an equilibration temperature well above the temperature of the N_2 ice, CH_4 will condense in areas of the surface which are too warm for the condensation of N_2. Additionally, the downward mass fluxes in Fig. 4b are a fair fraction of the thermal emission equivalent mass flux in Fig. 6. Because of this, condensation of CH_4 will slightly raise surface temperatures, which would tend to inhibit co-condensation of N_2.
6. We have ignored simultaneous heat and mass transport. In order to account for the fact that CH_4 patches can heat the atmosphere as well as add CH_4 to it, the flux in equation (5) would have to be the flux of virtual heat, which includes both the sensible heat flux and the mass flux, rather than simply the mass flux. Also, a separate scale factor for virtual temperature would have to be introduced. The effect of including the flux of sensible heat along with the mass flux we have calculated would be to increase upward mass flux rates and decrease downward fluxes. This is straightforward to see because upward fluxes of either heat or CH_4 result in the creation of buoyancy, so the flux of both CH_4 and heat from areas where CH_4 is sublimating and the atmosphere is being heated (i.e. CH_4 patches) will be enhanced relative to the value computed assuming that only one type of surface–atmosphere exchange is occurring. By leaving out the heat flux in these calculations we have made a somewhat conservative estimate of the contrast between the upward and downward CH_4 mass fluxes.

All of the mechanisms discussed here should apply to Triton as well as Pluto, although their current seasonal states are quite different. Triton's atmospheric composition is $\chi = 10^{-4}$, which is about the value expected from the ratio of the CH_4 vapor pressure to that of N_2. However, spectroscopy of Triton's surface ices (Cruikshank *et al.*, 1993; Brown *et al.*, 1995; Quirico and Schmitt, 1996) reveals no evidence of an unshifted (pure) CH_4 band such as is seen on Pluto. The spectra also indicate that the CH_4 is present at a very low concentration ($\sim 0.1\%$) in the solid solution, a factor of the order of 10 lower than on Pluto. Using Raoult's law the predicted mixing ratio of CH_4 in Triton's atmosphere is 10^{-7}, three orders of magnitude smaller than what has been observed. This suggests that the CH_4 mixing ratio in both atmospheres is considerably elevated. Since χ is much lower on Triton than on Pluto, the fraction of the surface we would need to have covered by CH_4 patches would also be much smaller than the few percent we calculate for Pluto. It is easy to imagine that the patches would be difficult to detect on Pluto, and much harder to find on Triton. It should be noted that the detailed balancing model of Trafton (1990) (see also Spencer *et al.* (1996)) is also consistent with the different atmospheric compositions of Triton and Pluto, so this does not provide a discriminating test of the two models.

There are a number of ways in which this model can be tested, either now or in the future. Further laboratory work on the sublimation of N_2:CH_4 solid solutions as well as their condensation will help resolve some of the uncertainty about whether CH_4 forms a grainy layer or a detailed balancing layer under conditions more like those on Triton and Pluto. Detection of the appearance of a pure CH_4 feature in the spectrum of Triton accompanied by a change in the thermal structure of its atmosphere, or the opposite on Pluto, would be at least a qualitative confirmation of this model because it predicts the possibility of seasonal variations in the composition of the atmospheres of both bodies. However, prediction of the timing of the changes and their magnitude is probably beyond the scope of our current understanding of either body. The effect of declining surface pressure, driven by Pluto's eccentricity, would be different in the two models. In this model, the atmospheric composition could become more CH_4 rich as the total pressure declines, leading to potentially greater atmospheric heating. In the detailed balancing model the atmospheric composition is basically constant in time. Presumably this would result in a steadily decreasing upper atmospheric temperature as Pluto recedes from the Sun, regardless of the surface pressure. Stansberry *et al.* (1995) find that Pluto's atmospheric pressure will drop to 4.2 μb within approximately 20 years. If the current pressure is 58 μb, this represents a change by a factor of 10. If the CH_4 partial pressure remains at current levels over that time, the resultant mixing ratio will be 10% rather than 1%, which would have marked effects on the atmospheric temperature structure. Fortuitous occultations or a spacecraft mission should be able to detect changes of this magnitude, as could the direct method used by Young (1994) for measuring the CH_4 abundance in Pluto's atmosphere.

Acknowledgements. Support by the National Research Council Fellowship Program is gratefully acknowledged by J.A.S. and R.V.Y. Additional funding was provided through NASA grants

NAGW-1039 (J.I.L.), NAGW-3395 (J.A.S., J.R.S.), and by the Friends of Lowell Observatory (J.A.S.). Laboratory work in France was supported by the French Programme National de Planétologie of the Institut National des Sciences de l'Univers. The authors thank Emmanuel Lellouch and Larry Trafton for their thoughtful reviews. Larry Trafton also provided many vigorous discussions, which greatly improved both the model and the paper. Jane Spencer elucidated the phase similarities between a sublimating N_2:CH_4 solid solution and beer bubbles. We thank Eric Quirico for his assistance with the lab data.

References

Altenhoff, W. J., Chini, R., Hein, H., Kreysa, E., Mezger, P. G., Salter, C. and Schraml, J. B., First radio astronomical estimate of the temperature of Pluto. *Astron. Astrophys.* **190**, L15–L17, 1988.

Arya, S. P., *Introduction to Micrometeorology*. Academic Press, San Diego, 1988.

Blumsack, S. L., Gierasch, P. J. and Wessel, W. R., An analytical and numerical study of the Martian planetary boundary layer over slopes. *J. Atmos. Sci.* **30**, 66–82, 1973.

Brown Jr, G. N. and Ziegler, W. T., Vapor pressure and heats of vaporization and sublimation of liquids and solids of interest in cryogenics below 1-atm pressure. *Adv. Cryogenic Engng* **25**, 662–670, 1980.

Brown, R. H., Cruikshank, D. P., Veverka, J., Helfenstein, P. and Eluszkiewicz, J., Surface composition and photometric properties of Triton, in *Neptune and Triton* (edited by D. P. Cruikshank). University of Arizona Press, Tucson, 1995.

Buie, M. W., Tholen, D. J. and Horne, K., Albedo maps of Pluto and Charon: initial mutual event results. *Icarus* **97**, 211–227, 1992.

Businger, J. A., Wyngaard, J. C., Izumi, Y. and Bradley, E. F., Flux–profile relationships in the atmospheric boundary layer. *J. Atmos. Sci.* **28**, 181–189, 1971.

Cruikshank, D. P., Roush, T. L., Owen, T. C., Geballe, T. R., de Bergh, C., Schmitt, B., Brown, R. H. and Bartholomew, M. J., Ices on the surface of Triton. *Science* **261**, 742–745, 1993.

Cruikshank, D. P., Roush, T. L., Quirico, E., Owen, T. C. and de Bergh, C., Surface composition of Triton, Pluto, and Charon, in *Ices in the Solar System Conference*, Toulouse, France, 1995.

Cruikshank, D. P., Roush, T. L., Moore, J. M., Sykes, M. V., Owen, T. C., Bartholomew, M. J., Brown, R. H. and Tryka, K. A., The surfaces of Pluto and Charon, in *Pluto and Charon* (edited by D. J. Tholen and S. A. Stern). University of Arizona Press, Tucson, 1996.

Drish Jr, W. F., Harmon, R. H., Marcialis, R. L. and Wild, W. J., Images of Pluto generated by matrix lightcurve inversion. *Icarus* **113**, 360–386, 1995.

Elliot, J. L. and Young, L. A., Analysis of stellar occultation data for planetary atmospheres. I. Model fitting with application to Pluto. *Astron. J.* **103**, 991, 1992.

Elliot, J. L., Dunham, E. W., Bosh, A. S., Slivan, S. M., Young, L. A., Wasserman, L. H. and Millis, R. L., Pluto's atmosphere. *Icarus* **77**, 148–170, 1989.

Eluszkiewicz, J., On the microphysical state of the surface of Triton. *J. Geophys. Res.* (*Suppl.*) **96**, 19217–19229, 1991.

Flasar, F. M. and Goody, R. M., Diurnal behaviour of water on Mars. *Planet. Space Sci.* **24**, 161–181, 1976.

Grundy, W. M. and Fink, U., Synoptic CCD spectrophotometry of Pluto over the past 15 years. *Icarus* 1996 (in press).

Grundy, W. M., Schmitt, B. and Quirico, E., The temperature-dependent spectra of α and β nitrogen ice with application to Triton. *Icarus* **105**, 254–258, 1993.

Hubbard, W. B., Hunten, D. M., Dieters, S. W., Hill, K. M. and Watson, R. D., Occultation evidence for an atmosphere on Pluto. *Nature* **336**, 452–454, 1989.

Hubbard, W. B., Yelle, R. V. and Lunine, J. I., Nonisothermal Pluto atmosphere models. *Icarus* **84**, 1–11, 1990.

Ingersoll, A. P., Dynamics of Triton's atmosphere. *Nature* **344**, 315–317, 1990.

Ingersoll, A. P. and Tryka, K. A., Triton's plumes: the dust devil hypothesis. *Science* **250**, 435–437, 1990.

Jewitt, D. C., Heat from Pluto. *Astron. J.* **107**, 372–378, 1994.

Leighton, R. R. and Murray, B. C., Behavior of CO_2 and other volatiles on Mars. *Science* **153**, 136–144, 1966.

Lellouch, E., The thermal structure of Pluto's atmosphere: clear vs. hazy models. *Icarus* **108**, 255–264, 1994.

Lunine, J. I. and Stevenson, D. J., Physical state of volatiles on the surface of Triton. *Nature* **317**, 238–240, 1985.

Millis, R. L., Wasserman, L. H., Franz, O. G., Nye, R. A., Elliot, J. L., Dunham, E. W., Bosh, A. S., Young, L. A., Slivan, S. M., Gilmore, A. C., Kilmartin, P. M., Allen, W. H., Watson, R. D., Dieters, S. W., Hill, K. M., Giles, A. B., Blow, G., Priestley, J., Kissling, W. M., Walker, W. S. G., Marino, B. F., Dix, D. G., Page, A., Ross, J. E., Kennedy, H. D. and Klemola, A. R., Pluto's radius and atmosphere: results from the entire 9 June 1988 occultation data set. *Icarus* **105**, 282–297, 1993.

Owen, T. C., Roush, T. L., Cruikshank, D. P., Elliot, J. L., Young, L. A., de Bergh, C., Schmitt, B., Geballe, T. R., Brown, R. H. and Bartholomew, M. J., Surface ices and atmospheric composition of Pluto. *Science* **261**, 745, 1993.

Prokhvatilov, A. I. and Yantsevich, L. D., X-ray investigations of the equilibrium phase diagram of CH_4–N_2 solid mixtures. *Sov. J. Low Temp. Phys.* **9**, 94–97, 1983.

Quirico, E. and Schmitt, B., Near infrared spectroscopy of simple hydrocarbons and carbon oxides diluted in solid N_2 and as pure ices: implication for Triton and Pluto. *Icarus* 1996 (in press).

Quirico, E., Schmitt, B., Bini, R. and Salvi, P. R., Spectroscopy of some ices of astrophysical interest: SO_2, N_2 and N_2:CH_4 mixtures. *Planet. Space Sci.* **44**, 973–986, 1996a.

Quirico, E., Schmitt, B., Doute, S., Grundy, W., de Bergh, C., Cruikshank, D. P., Roush, T. L., Owen, T. C. and Geballe, T. R., *Icarus* 1996b (in preparation).

Reid, R. C., Prausnitz, J. M. and Sherwood, T. K., *Properties of Gases and Liquids*. McGraw-Hill, New York, 1977.

Schmitt, B., de Bergh, C., Lellouch, E., Maillard, J. P., Barbe, A. and Doute, S., Identification of three absorption bands in the two micron spectrum of Io. *Icarus* **111**, 79–105, 1994.

Schmitt, B., Quirico, E., Doute, S., Grundy, W., de Bergh, C., Cruikshank, D. P., Roush, T. L., Owen, T. C. and Geballe, T. R., Evidence of a vertical stratification of methane at the surface of Pluto. *Icarus* 1996 (in preparation).

Spencer, J. R., Nitrogen frost migration on Triton: a historical model. *Geophys. Res. Lett.* **17**, 1769–1772, 1990.

Spencer, J. R., Stansberry, J. A., Trafton, L. M., Young, E. F., Binzel, R. P. and Croft, S. K., Volatile transport, seasonal cycles, and atmospheric dynamics on Pluto, in *Pluto and Charon* (edited by S. A. Stern and D. J. Tholen). University of Arizona Press, Tucson, 1996 (in press).

Stansberry, J. A., Surface–atmosphere coupling on Triton and Pluto, Ph.D. Dissertation, University of Arizona, Tucson, 1994.

Stansberry, J. A., Lunine, J. I. and Tomasko, M. G., Upper limits on possible photochemical hazes on Pluto. *Geophys. Res. Lett.* **16**, 1221–1224, 1989.

Stansberry, J. A., Yelle, R. V., Lunine, J. I. and McEwen, A. S., Triton's surface–atmosphere energy balance. *Icarus* **99**, 242–260, 1992.

Stansberry, J. A., Lunine, J. I., Hubbard, W. B., Yelle, R. V. and Hunten, D. M., Mirages and the nature of Pluto's atmosphere. *Icarus* **111**, 503–513, 1994.

Stansberry, J. A., Yelle, R. V. and Pisano, D. J., A climatic conundrum in the outer solar system: emissivity and the nitrogen α–β transition. A presentation at the *Ices in the Solar System Conference*, Toulouse, France, 1995.

Stansberry, J. A., Pisano, D. J. and Yelle, R. V., The emissivity of volatile ices on Triton and Pluto. *Planet. Space Sci.* **44,** 945–955, 1996.

Stern, S. A., Weintraub, D. A. and Festou, M. C., Evidence for a low surface temperature on Pluto from millimetre-wave thermal emission measurements. *Science* **261,** 1713–1716, 1993.

Strobel, D. F., Zhu, X. and Summers, M. E., On the vertical thermal structure of Pluto's atmosphere. *Icarus* **120,** 266–289, 1996.

Sutton, J. L., Loevy, C. B. and Tillman, J. E., Diurnal variations of the Martian surface layer meteorological parameters during the first 45 sols at two Viking Lander sites. *J. Atmos. Sci.* **35,** 2346–2355, 1978.

Sykes, M. V., Cutri, R. M., Lebofsky, L. A. and Binzel, R. P., IRAS Serendipitous observations of Pluto and Charon. *Science* **237,** 1376–1440, 1987.

Trafton, L., Large seasonal variations in Triton's atmosphere. *Icarus* **58,** 312–324, 1984.

Trafton, L., A two-component volatile atmosphere for Pluto. I. The bulk hydrodynamic escape regime. *Astrophys. J.* **359,** 512–523, 1990.

Trafton, L. and Stern, S. A., On the global distribution of Pluto's atmosphere. *Astrophys. J.* **267,** 872–881, 1983.

Tryka, K. A., Brown, R. H., Cruikshank, D. P., Owen, T. C., Geballe, T. R. and de Bergh, C., Temperature of nitrogen ice on Pluto and its implications for flux measurements. *Icarus* **112,** 513–527, 1994.

Yelle, R. V. and Lunine, J. I., Evidence for a molecule heavier than methane in the atmosphere of Pluto. *Nature* **339,** 288–290, 1989.

Yelle, R. V., Lunine, J. I., Pollack, J. B. and Brown, R. H., Lower atmospheric structure and surface–atmosphere interactions on Triton, in *Neptune and Triton* (edited by D. P. Cruikshank). University of Arizona Press, Tucson, 1995.

Young, L. A., Bulk properties and atmospheric structure of Pluto and Charon, Ph.D. Dissertation, Massachusetts Institute of Technology, 1994.

Young, E. L. and Binzel, R. P., A new determination of radii and limb parameters for Pluto and Charon from mutual event lightcurves. *Icarus* **108,** 219–224, 1994.