RHEOLOGY OF SOLID METHANE AND NITROGEN: APPLICATIONS TO TRITON

Janusz Eluszkiewicz and David J. Stevenson
Division of Geological and Planetary Sciences
California Institute of Technology

ABSTRACT: The existing information about the rheological properties of solid methane and nitrogen is reviewed. The main limitation is the absence of creep data for solid nitrogen, but estimated properties are derived on the basis of simple scaling arguments for van der Waals bonded materials. On Triton solid methane and most likely nitrogen are too soft to support any topography over billions of years. Topographic support by water ice-rich materials seems almost certain. Nitrogen and methane do not intermix by solution-state diffusion. The weakness (absence?) of the opposition effect on Triton can be explained by annealing of nitrogen grains, provided the latter have sizes characteristic of freshly deposited frost.

Introduction

The Voyager encounter with Triton has revealed a bewildering variety of geological structures [Smith et al. 1989]. The UV experiment onboard the spacecraft combined with Earth-based spectroscopical observations provide evidence that solid methane and nitrogen are the dominant constituents at least on the southern polar surface currently facing the Sun, although the very low partial pressure of CH₄ (sublimation by about a factor of 10, [Broadfoot et al. 1989]) in the atmosphere implies that the fractional coverage of Sun-facing regions covered with CH₄ must be low. An understanding of the rheological properties of these ices at low temperatures (the surface temperature on Triton is ~37 K) seems therefore to be a prerequisite in any attempt to explain Triton's morphology and history. The aim of this note is to summarize the existing data on rheology of CH₄ and N₂ ices and provide a preliminary assessment of the implications of these data. For methane this will lead to the construction of a deformation map. When used in homologous stress and temperature variables, this map should also have some applicability for nitrogen, for which no creep data exist. Although there exists no definite proof of this, it seems plausible that materials of similar crystal structure and molecular bonding should have similar deformation maps in these coordinates. Both nitrogen and methane are van der Waals-bonded solids. Based on the rheological information so obtained we will then proceed to evaluate its importance in explaining three phenomena related to Triton: 1. Intermixing of methane and nitrogen and its implications for volatile redistribution; 2. The preservation of topography; and 3. The weakness of the opposition effect.

Construction of the deformation maps

In modeling the flow phenomena on planetary surfaces the first step is to identify the mechanisms involved in deformation. The total strain-rate is then the sum of contributions from individual mechanisms. The main deformation mechanisms are [Ashby and Verrall 1978]:

1. Cataclastic flow caused by repeated cleavage fracture and rolling of already fractured fragments. In this paper this process will be characterized by a single parameter, the fracture strength \( \sigma_f \).

2. Low temperature plasticity. Although not usually considered a steady-state mechanism, this process is included here to determine the onset of time-dependent deformation, with the corresponding yield stress \( \sigma_y \).

3. Diffusional flow, including volume (Nabarro-Herring) and boundary (Coble) diffusion. The corresponding flow is Newtonian viscous. The associated strain-rate is \( \dot{\varepsilon}_f = 42D_{\text{eff}} \varepsilon \Omega k T d^3 \), where \( D_{\text{eff}} = D_V [1 + (x d)(D_B/D_V)] \), \( D_V = D_V \exp(-E_V/RT) \), and \( D_B = D_0 \exp(-E_B/RT) \) are the effective, volume, and boundary diffusivities, respectively. \( E_V \) and \( E_B \) are the corresponding activation energies, \( \varepsilon \) is the deviatoric stress, \( T \) temperature, \( \Omega \) the molecular volume, \( k \) the Boltzmann constant, \( R \) the universal gas constant, \( d \) the grain size, and \( \delta \) the thickness of the boundary diffusion path.

4. Power-law creep, with strain-rate commonly expressed as \( \dot{\varepsilon}_c = A \sigma^m \exp(-Q_c/RT) \).

5. Other processes, e.g., pressure solution creep and creep aided by dynamic recrystallization. These processes are less well understood and moreover their importance for Triton is difficult to assess. They will therefore be excluded from the present considerations, which leads to an underestimate of the total strain-rate. However, it is shown below that deformation by power-law creep alone is in most cases geologically rapid so this omission is unlikely to cause severe problems.

Except for cataclastic flow, deformation is largely independent of pressure at the modest pressures of interest. This leads to a convenient way of displaying rheological properties of a material in the form of deformation maps. A deformation map shows regions in the \( \dot{\varepsilon},T \)-plane in which a particular deformation mechanism dominates. The boundaries between regions are found by equating the strain-rates for each pair of mechanisms and solving the resulting equations for the function \( \dot{\varepsilon}(T) \). On those boundaries are superimposed contours of constant strain-rate, given by equations of the form \( \dot{\varepsilon} = \text{const} = f(\sigma, T) \). The homologous coordinates are \( \sigma \mu \) and \( T/T_m \), where \( \mu \) is the shear modulus and \( T_m \) is the melting temperature.

Methane

Rheological data for methane are more complete than for
nitrogen. The fracture strength has been measured by Haynes [1971] at \( T = 77 \) K with the result \( \sigma_f = 7.46 \) bar. In the deformation maps the line \( \sigma = \sigma_f \) is taken as the boundary above which flow takes place by repeated fracture. The possible dependence of \( \sigma_f \) on \( T \) is neglected but this is unlikely to be a serious limitation, especially an a log-log plot. The yield stress of methane was determined in the 40-50 K range relevant to Triton by Leonteia et al. [1970], \( \sigma_f \approx 5 \) bar. The parameters for volume diffusion, obtained from an analysis of the measurements of the spin-lattice relaxation time \( T_1 \) in the NMR experiments, are \( D_{ov} = 10^{-3} \text{m}^2/\text{s} \) and \( E_v = 15.9 \text{kJ/mole} \) [Chezeau and Strange 1979]. The molecular volume is \( \Omega = 5.11 \times 10^{-29} \text{m}^3 \). No data for boundary diffusion exist and therefore following the suggestion by Ashby and Verall [1978] the scaling \( E_b = 2/3 E_v \) and \( \delta D_{ob} = 10^{-9} D_{ov} \) (in SI units) will be used. The creep parameters at temperatures relevant to Triton have been measured by Bolshutkin et al. [1968]: \( n = 3 \), \( Q_c = 8.4 \text{kJ/mole} \), and \( A = 10 \text{MPa}^{-3} \text{s}^{-1} \). Two words of caution are in order concerning these values. First, they were obtained at strain-rates not lower than \( 10^{-7} \text{s}^{-1} \) and thus their application to geological processes may require extrapolations over many orders of magnitude in strain-rate. Second, the value of \( A \) is not given in the Soviet paper and had to be estimated. This estimation was rendered difficult as the authors do not report the length of their specimens. Based on a comparison with other experiments done by the same group we have come to the conclusion that plausible range of specimen length results in the above value of \( A \) being multiplied by a numerical factor between 0.8 and 1.3. Our choice is a compromise between these extremes.

![Deformation map for solid methane for grain size \( d = 0.1 \text{mm} \).](image)

Fig. 1. Deformation map for solid methane for grain size \( d = 0.1 \text{mm} \). The thin lines are contours of constant strain-rate labeled by the value of \( \log_{10}(\epsilon) \), where \( \epsilon \) is the strain rate in \( \text{s}^{-1} \). This map may also be applicable to solid nitrogen in the homologous coordinates \( \sigma/\mu \) and \( T/T_m \) (\( \mu \) is the shear modulus and \( T_m \) the melting temperature).

A deformation map constructed from the above data is shown in Figure 1 for the grain size \( d = 0.1 \text{mm} \). Nothing is known about the latter in Triton's subsurface layers. Zent et al. [1989] argue in favor of meter-sized grains, but the validity of their argument has been brought into question by Kirk [1990]. The melting temperature of methane at zero pressure is \( T_m = 90.67 \text{K} \) and the shear modulus is \( \mu = 20 \text{bar} \) [Bezuglyi et al. 1966]. For comparison, the shear modulus of water ice is \( \mu = 35 \text{bar} \) [Gammon et al. 1983]. The lower value of \( \mu \) for \( \text{CH}_4 \) is consistent with weaker molecular bonding in solid methane. From Figure 1 it can be seen that power-law creep is indeed the dominant deformation mechanism, even for small grain sizes. Diffusional processes only become important at small grain sizes and stresses lower than 0.1 bar, which correspond to \( \sim 20 \) m topography on Triton. For this reason and because the main topographic relief on Triton is \( \sim 1 \text{km} \), the uncertainty in grain size has no major impact on the conclusions of this paper with regard to the relaxation of topography. The fracture field is separated by only a narrow plasticity region from the creep field and it is therefore possible that cataclastic flow might be associated with the highest topography on Triton. Lithospheric stresses corresponding to 1 km topography are on the order of 4.6 bar.

As noted above, it is difficult to establish whether any additional deformation processes operate in Triton's surface layers. Pressure solution creep requires the presence of liquid in the pores which given Triton's low temperatures seems unlikely for at least the upper few kilometers. Concerning dynamic recrystallization, nothing is known about the role, if any, of the formation of preferred texture in the flow of solid methane. Only future experimental efforts can shed light on this issue.

### Nitrogen

The rheological data for nitrogen are much more scarce. Neither the fracture strength nor the yield stress have been measured. However, both are unlikely to be very different from methane's, given the similarity of the two materials in terms of crystal structure and molecular bonding. This point is corroborated by the observation that the shear modulus of nitrogen has a value very close to the value of methane [Scott 1976]. The only direct rheological data are for volume diffusion [Esteve and Sullivan 1981]: \( D_{ov} = 16 \times 10^{-8} \text{m}^2/\text{s} \), \( E_v = 8.6 \text{kJ/mole} \). Given such meager information, the best way of describing rheology of nitrogen is by using the deformation map of methane in the homologous coordinates. Such procedure can be justified by the above mentioned similarity of the two ices and is rendered particularly appealing by the coincidence of shear moduli. Given that the zero-pressure melting temperature \( T_m = 63.148 \text{K} \) of \( \text{N}_2 \) is lower than for \( \text{CH}_4 \), nitrogen can be expected to be much softer than methane at any particular stress and temperature.

### Consequences

**Nitrogen and methane - no solid-state interdiffusion**

The first question which can be addressed using the data given above is the degree to which nitrogen and methane can be intermixed by solid-state diffusion. This is a potentially important issue as it relates to the problem of volatile redistribution in the last \( \sim 3.5 \text{Gyr} \), i.e., since the end of the intense tidal heating associated with circularization of Triton's orbit [McKinnon 1984, Goldreich et al. 1989]. In addition, large amounts of nitrogen well mixed with methane would considerably soften rheology and aggravate the problem of preserving topography in nonwater ices. While there is no prospect at present to calculate the relative proportions of
nitr came and methane on Triton, the degree to which they can interdiffuse can be estimated very simply. The upper limit on the coefficient of interdiffusion $D^*$ in an $n$-phase system is given by the diffusivity of the fastest component. In the methane-nitrogen system the highest possible value is given by $D^* = D(N_2)$. In this case the mean square path $\langle D^* t \rangle^{1/2}$ over $t = 3.5$ Gyr is only 1 $\mu$m at 37 K and 5 cm at 63.148 K.

Methane and nitrogen, once separated, cannot be mixed in solid state by diffusion alone (a thermally driven separation may have occurred because $N_2$ is preferentially volatilized with respect to $CH_4$). This is consistent with the disequilibrium assemblage preferred by Lunine and Stevenson [1985]. On the other hand, the generally short diffusion paths do not exclude the possibility of large grains advocated by Zent et al. [1989], since at the relevant temperatures grain growth most likely occurs through vapor transport.

Relaxation of topography

The discovery of a well preserved and diversified topography on Triton prompted the question whether such topography can survive over geological time in the two directly observable components of Triton’s surface, $CH_4$ and $N_2$. If this turns out to be impossible, then the natural implication will be that the layer of these ices is thin and topography is supported by water ice. From Figure 1 it is immediately clear that the highest observed topography of ~1 km cannot be supported by methane ice alone (as mentioned above nitrogen fares even worse in this regard). Such topography corresponds to lithostatic stresses of ~4.6 bar and in the 40-50 K range to strain-rates $\dot{\varepsilon} \sim 10^{-12}$ - $10^{-10}$ s$^{-1}$. The Rayleigh-Taylor relaxation time for a thin constant viscosity layer is [Panelsker and Head 1981]

$$\tau = \frac{(3/4\pi^2)(h/D)(\lambda/D)^2}{\lambda}$$

where $h$ is the height of the topography, $\lambda$ its horizontal wavelength, and $D$ the thickness of the methane layer. In Figure 2 the wavelength of topography for which $\tau = 3.5$ Gyr is plotted as a function of $D$. Only values $D$ greater than $h$ should be considered since otherwise the estimate (1) ceases to be meaningful. It is evident that only long-wavelength topography has any chance of surviving over several billion years, e.g., for $T = 40$ K and $D = 100$ m, $\lambda = 100$ h, whereas for $D = 10$ km, $\lambda = 10^3$ h is required to achieve this. For $T = 90$ K (which may correspond to regions of lower albedo), already for $D = 100$ m only topography with $\lambda$ greater than $1000$ h can survive. For $T = 60$ K, no kilometer-scale topography can survive over 3.5 Gyr. Such estimates, despite their limitations, allow several conclusions:

1. Short-wavelength topography such as cliffs and ridges either formed recently or is supported by water ice.

2. The largest observed impact crater ($\lambda = 27$ km) could be preserved in methane only if the methane layer is significantly thinner than 1 km and the subsurface temperatures are low ($T \sim 40$ K). In fact, this is unrealistic, since such a large crater would excavate below the thin methane layer. Also, if the viscosity decreases with depth, the long wavelength components will relax away faster than predicted by Eq. (1).

Thus it seems almost certain that topography is supported by a water-based ice (e.g., ordinary water ice, ammonia hydrate or clathrate).

**Fig. 2.** The ratio of the wavelength of topography to topographic height $\lambda/h$ for topography which can be supported over 3.5 Gyr by a layer of solid methane as a function of layer thickness $D$. Only values $h$ much smaller than $D$ should be considered. The curves are labeled by the values of temperature at the base of the methane layer. Owing to $n = 3$ in the creep law, the curves are independent of $h$ in these coordinates.

The opposition effect (or lack thereof?)

The opposition effect is defined as an enhancement in the logarithmic brightness of an object when observed at phase angles $\leq 7^\circ$, in excess of that predicted by a linear extrapolation of the brightness vs phase relation from larger phase angles. Ground-based observations combined with Voyager data suggest that the opposition effect on Triton is very weak or absent [Smith et al. 1989]. As this effect is usually associated with the porous structure of the optically active layer, a possible explanation would involve pressureless sintering of the uppermost layers. This process would be most efficient in the nitrogen frost. The rate at which this surface-tension driven sintering proceeds is given by the formula [Ashby 1988]

$$\dot{\phi} = 72C(1-\phi_0)D\gamma\Omega/kTd^3$$

where $\phi_0$ and $\phi$ are the starting and actual porosity, respectively, $C = \phi_0/\phi_0(\phi_0 - \phi)$, and $\gamma$ is the surface energy. Given the similarity of elastic moduli of nitrogen and water ice, it seems plausible to adopt for nitrogen $\gamma = 0.1$ J m$^{-2}$, the value for water ice. Assuming $\phi_0 = 0.36$, $\phi = 0.3$ and using diffusion data for nitrogen, one obtains the timescale for compaction at $T = 37$ K, $c_c$ [s] = $-\phi/\phi = 5 \times 10^2$ (d/1 m)$^3$. For annealing to proceed on a timescale of Triton’s seasons ($c_c \sim 10^2$ yr), d smaller than 20 $\mu$m is required. While this is a plausible range of grain sizes for freshly deposited frost, the possibility of a rapid grain growth [Zent et al. 1989] presents a complicating factor (it is worth noting that grain growth by itself does not remove porosity and thus should not contribute to the decrease in the opposition surge). We conclude that sintering offers a speculative explanation at best for the weakness of the opposition effect. Recent reevaluation of the ground-based observations suggests that the opposition effect, while weaker than for other icy satellites, is present on Triton after all (A. Harris, personal communication). New
observations would be of paramount help in clarifying the picture.

Summary

Based on the existing rheological data it is concluded that on Triton solid methane and most likely nitrogen are too soft to support any topography over billions of years. Topographic support by water ice-rich materials seems almost certain. Nitrogen and methane do not intermix by solid-state diffusion. The weakness (absence?) of the opposition effect on Triton can be explained by annealing of nitrogen grains, provided the latter have sizes characteristic of freshly deposited frost. Recommendations for further research include: 1. Creep measurements of solid nitrogen; 2. Better understanding of grain growth in solid nitrogen; 3. Clarification of the opposition behavior.

Acknowledgements. Thanks are due to Bill McKinnon and two anonymous referees for their careful reading of the manuscript and helpful comments. This work has been supported by the NASA Planetary Geophysics Grant NAGW-185. Contribution number 4881 from the Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, California 91125.

References


Janusz Eluszkiewicz and David J. Stevenson, Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125, USA.

(Received March 29, 1990; revised June 18, 1990; accepted June 20, 1990.)