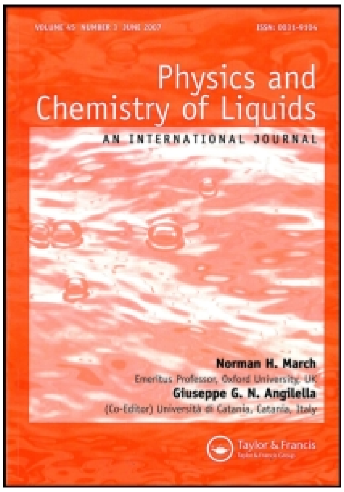

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Is the brittle-ductile transition preceding melting related to 5- and 7-membered ring defects in graphite?

D. J. Klein[a]; N. H. March[bc]
[a] Texas A&M University @ Galveston, Galveston, Texas, USA [b] Department of Physics, University of Antwerp, Antwerp, Belgium [c] Oxford University, Oxford, England

To cite this Article Klein, D. J. and March, N. H.(2007) 'Is the brittle-ductile transition preceding melting related to 5- and 7-membered ring defects in graphite?', Physics and Chemistry of Liquids, 45: 6, 609 — 613
To link to this Article: DOI: 10.1080/00319100701491163
URL: http://dx.doi.org/10.1080/00319100701491163

Physics and Chemistry of Liquids
Vol. 45, No. 6, December 2007, 609–613

Taylor & Francis
Taylor & Francis Group

Is the brittle–ductile transition preceding melting related to 5- and 7-membered ring defects in graphite?

D. J. KLEIN*† and N. H. MARCH‡§

†Texas A&M University @ Galveston, Galveston, Texas 77553, USA
‡Department of Physics, University of Antwerp, Antwerp, Belgium
§Oxford University, Oxford, England

(*Received 15 April 2007; in final form 3 June 2007*)

The brittle–ductile transition (BDT) is a very general phenomenon in materials science. The temperature T_{BDT} in numerous materials correlates somewhat with the higher melting temperature T_{m}. We have earlier proposed the disclination (or rotation-dislocation) as a universal ingredient in the BDT. The present study is exclusively concerned with graphite, where $T_{\mathrm{m}} \approx 4000\,\mathrm{K}$. Our conclusion is that the energetics of 5- and 7-membered rings play a crucial role in determining these temperatures. However, experiment is to be invoked, should T_{BDT} eventually be measured for graphite, so as to decide between various mechanisms, all of which here depend on 5- and 7-membered rings. One mechanism involves interlayer van der Waals coupling, whence a pressure experiment may hold the key.

Keywords: brittle-ductile transition; dislocations; disclinations; melting; graphite

1. Introduction

Graphite is extremely unusual for several reasons, e.g., with regard to the extreme high strength of its covalent bonds and its simultaneous extreme anisotropy, such as here, are relevant in its melting. In earlier work [1,2], we have proposed an interpretation to the melting and also the precursor brittle–ductile transition (BDT) in graphite in terms of dislocations and disclinations (or rotation-dislocations). Here, we estimate the transition temperature T_{BDT} from available knowledge of the energies per 5- and 7-fold rings embedded in graphite. Our estimates suggest a picture of the BDT with largely independent dislocations of paired 5- and 7-fold rings in the brittle (B) phase. Following the BDT transition, the dislocation concentration and mobility increases so that they frequently collide to lose their individual identity. Melting in graphite is then interpreted as a dislocation-mediated transition with a melting temperature T_{m} such that the corresponding thermal energy $k_{\mathrm{B}}T_{\mathrm{m}} \sim Gb^3$ where G is the shear modulus of the graphite and b is the Burger's vector.

---

*Corresponding author. Email: kleind@tamug.edu

Physics and Chemistry of Liquids
ISSN 0031-9104 print/ISSN 1029-0451 online
DOI: 10.1080/00319100701491163

In an earlier study [1], we have given evidence that in directionally bonded systems, such as transition metals and especially the covalently bonded networks of both graphite (sp^2-hybridized) and silicon (sp^3-hybridized), dislocations (translational) and disclinations (or rotation dislocations) are topological defects involved in the melting phase transition and in the precursor BDT. However, since some amorphous solids also exhibit BDTs, "simple" dislocations cannot be the universal ingredient of the BDT, so that we were led to focus on disclinations in [1]. We note that Langer and Pechenik [3] also excluded (translational) dislocations, though they did not mention disclinations.

In [1] and [2], some attention was already given to graphite, and this is now the prime focus of the present article. Crucial to our discussion subsequently is the experiment of Togoya [4] who showed that (i) the melting temperature $T_m \approx 4000\,\mathrm{K}$ over a substantial pressure range from ambient pressure on up. And also of relevance is the theoretical work of Seung and Nelson [5], concerned with the energetics of single disclinations, using elasticity theory.

2. Characteristic processes and energies

The bond energy for graphite is $\sim$5 eV, so that even for a transition at $\approx$4000 K one seeks lower energy excitations than those due to vacancies. Preferably, the defects result from rearrangements of atoms such as to avoid dangling bonds finally. Perhaps, the simplest such local rearrangement is that resulting from the "Stone–Wales" transformation [6], as indicated in figure 1. In a simplistic description this entails breaking external bonds to neighbor atoms, rotating the pair through 90°, and then reforming the bonds now to the same neighbor atoms but cyclically related to the initial pair. In mechanistic detail the bonds to external neighbors are not all fully broken and the detailed pathway the atoms follow is not so simplistic. Indeed for a single graphene sheet, it seems that there are different ideas as to the mechanism [7], with one [8] having one of the two atoms of the "rotating" pair break its external bonds, lift up out of the plane before the other atom moves, whereafter, the lifted atom resettles at another location in the plane – all with a rather high-activation energy of $\sim$9 eV. Another has a simpler rotation breaking two external bonds, starting the rotation of the pair

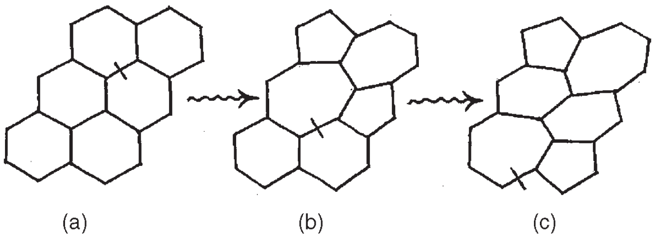
(a) (b) (c)

Figure 1. A portion of an undefected graphene sheet in (a), changing through rearrangement at the marked bond to give the defect of (b), which further can change through rearrangement at the new marked bond (of (b)) to give the defect of (c) with the two 7/5-pairs separated a little. Further separation can occur via further transformation, say at the bond marked in (c).

of atoms, while condensing the internal bond to a triple bond, and then continuing on to the final state – with an activation energy of ~8 eV. But of course graphite does not consist of isolated graphene sheets. We propose that the Stone–Wales rearrangement is much more facile in bulk graphite, where temporary bonds are formed normal to the graphene sheet to atoms in adjacent sheets without so severe a cost of bond breaking as that for a single sheet. Of the two rotated atoms each can form temporary bonds to opposite adjacent sheets. Two pairs of 5- and 7-membered rings result from this Stone–Wales transformation in graphite, and on repeating it these two pairs, which are "oppositely" oriented, may be separated from one another as also indicated in figure 1.

The estimation of the net energy cost of the defect resulting from a Stone–Wales transformation is relevant. Tersoff [9] estimates a core energy cost for each 5-membered ring of ~3.5 eV and a core energy for each 7-membered ring ~1 eV. This energy for a 5-membered ring is obtained from Tersoff's computations on fullerenes (while that for the 7-membered ring is obtained from negatively curved "analogues"). But somewhat lower energies for the 5-membered ring are found by others – e.g., to obtain [10] a core energy of ~2 eV, from empirical force fields. Yet with 5- and 7-membered rings adjacent to one another, we believe that the core energy is even lower, due to some local cancellation of curvature stresses. Indeed, a better estimate of the core energy of a fused pair of 5- and 7-member rings should be the difference in heats of formation between azulene [11] and naphthalene [12] given as

$$\varepsilon^0_{5/7} \cong (1264.5 - 1232.5)\ \text{kcal mole}^{-1} = 32\ \text{kcal mole}^{-1} \cong 1.39\ \text{eV}.$$

Similarly for a second fused 5/7 pair fused to the first (as in figure 1(b)), we anticipate further cancellations, so that the energetic cost is substantially less than the sum of two such 1.39-eV energies – perhaps more similar to the core energy cost of just one member of a 5/7 pair.

Aside from the core energy cost of different local structures, there is a further cost of deforming the surrounding graphitic network to accommodate the defect. For a dislocation defect, standard ideas indicate that this should scale (e.g., as in Read [13]) with the square of the Burger's vector of the defect and with the logarithm of the diameter of the surrounding network. Moreover, as this can entail largely bond-angle deformation (which is easier to make than comparable bond-length deformations), this stress energy should be more closely related to the shear modulus G than to the bulk modulus. Here a lone fused 5/7 pair of rings is a dislocation, with a Burger's vector corresponding to the minimum possible, that of neighbor-atom spacing b. The pair of such 5- and 7-membered rings as result from pure graphite after one or more Stone–Wales transformations are such that the Burger's vectors for each 5- and 7-membered pair have opposite Burger's vectors, so that their net Burger's vector is 0 and the stress in the region surrounding the pair of ring pairs is negligible. Thus, the energy cost of two fused opposed 5/7-membered pairs at a separation of r should be

$$\varepsilon_{5/7-7/5}(r) \cong \varepsilon^0_{5/7-7/5} + A \cdot \ln r$$

with the positive constant A scaling $\sim Gb^2$.

At a finite defect density of such pairs of dislocations, there is a cut-off for the distance r considered between such pairs. That is, if the average distance between such pairs is R, then this becomes at least roughly a cut-off distance for r, since it is only for values of $r \ll R$ that such pairs are in fact well identifiable. Thus, above a certain concentration of pair defects (with net Burger's vector 0), one can expect that it is more proper to simply speak of dislocations, with a mean energy cost of $\varepsilon_{5/7-7/5}(R)$ with R a square root of the area of a sheet containing one defect – i.e., R is inversely proportional to the square-root of the density of the defects. Hence one might anticipate the possibility of a phase transition, where pair defects dissociate – such typically being termed a Kosterlitz–Thouless transition [14].

Granted dislocations, it is typically imagined that they occur along lines normal to the layers, with the (in-plane) Burger's vector conserved from one layer to the next. This guarantees that two successive layers are largely in registry with one another. But for the extremely anisotropic case of graphite, with successive layers corresponding to separate weakly interacting graphene sheets, one might entertain the possibility of dislocations in successive sheets not being correlated with one another. This brings the bulk of the sheets out of registry with one another, and costs a fraction of the van der Waals coupling between adjacent layers. But at the same time there would be a notable gain in entropy if dislocations in adjacent layers lose correlation. The loss of van der Waals energy is anticipated to be a just a few tenths of an eV per C atom, while the entropy gain is proportional to the logarithm of the number of ways to place the (equilibrium number of) dislocations randomly into the network. Ordinarily such decoherence of dislocations is not imagined because this energy cost per sheet is proportional to the total number of atoms in a sheet, while the entropy gain involves just the (much smaller) number of dislocations.

But in addition to the dislocations which are neighbor pairs of 5- and 7-membered rings, there are other possibilities. In particular, the 5- and 7-membered rings may be separated from one another avoiding dangling bonds, and placing one or more intervening hexagonal rings between the two. But well separated 5- and 7-membered rings are individually viewable as disclinations (or "rotation dislocations"), and for a separation of r they have [5,9] an energy

$$\varepsilon_{5-7}(r) \cong \varepsilon_5^0 + \varepsilon_7^0 + B \cdot \ln r$$

where ε_5^0 & ε_7^0 are core energies for the two disclinations and B is a constant scaling in proportion to the degree of curvature of the disclinations. Here, Tersoff [9] has made an estimate of these two core energies, but as from our discussion above, we anticipate that at least ε_5^0 may be too high by a factor of approximately 2.

The mode of transformation separating 5- and 7-membered disclination rings from one another is again *via* a Stone–Wales process [6]. We again propose that the activation energy for this is less for the case of graphite than for lone graphene sheets. Also it is significant that, *via* the Stone–Wales transformation, the separation of the 5- and 7-membered rings gives rise [1] to additional 5/7-dislocations.

Granted this formulation for dislocations consisting of disclination pairs, a dissociation into disclinations can be imagined, similar to the dissociation of local defects into dislocations. That is, there is a possibility to a soup (or plasma) of disclinations. The possibility of decoherence of disclinations between adjacent layers seems unlikely, in that if this were to be imagined, the severe conical or saddle distortions (with nonvanishing Gaussian curvature) for disclinations would entail even greater van der Waals energy loses – and especially pressure dependences contrary to Togoya's observations [4].

3. Outlook

In summary, all lines of thought presented in this article lead us to answer affirmatively the question posed in the title (concerning the relevance of 5- and 7-membered rings). Overall we anticipate $k_B T_{BDT}$ should be proportional to a characteristic energy, which may have different contributing factors as indicated in our discussion. Whether T_{BDT} depends on interlayer interactions is important. For a quantitative understanding several relevant energies remain to be more accurately estimated.

Acknowledgements

D. J. Klein acknowledges support (*via* grant BD-894) from the Welch Foundation of Houston, Texas. N. H. March wishes to thank Professor W. A. Seitz for generous hospitality during his visit to Texas A&M University at Galveston.

References

[1] D.J. Klein, N.H. March. *Phys. Chem. Liquids*, **42**, 545 (2004).
[2] N.H. March. *Phys. Chem. Liquids*, **44**, 477 (2007).
[3] J.S. Langer, L. Pechenik. *Phys. Rev. E*, **68**, 061507 (2003).
[4] M. Togoya. *Phys. Rev. Lett.*, **79**, 2474 (1997).
[5] H.S. Seung, D.R. Nelson. *Phys. Rev. A*, **38**, 1005 (1988).
[6] A.J. Stone, D.J. Wales. *Chem. Phys. Lett.*, **128**, 501 (1986).
[7] H. Bettinger, B.I. Yakobson, G.E. Scuseria . *J. Am. Chem. Soc.*, **125**, 5572 (2003).
[8] R.L. Murry, D.L. Strout, G.K. Odom, G.E. Scuseria. *Nature*, **366**, 665 (1993).
[9] J. Tersoff. *Phys. Rev.*, **46**, 15546 (1992).
[10] T.G. Schmalz, W.A. Seitz, D.J. Klein, G.E. Hite. *J. Am. Chem. Soc.*, **110**, 1113 (1988).
[11] E. Kovats, H.H. Gunthard, P.A. Plattner. *Helv. Chim. Acta.*, **38**, 1912 (1955).
[12] D.M. Speros, F.D. Rossini. *J. Phys. Chem.*, **64**, 1723 (1960).
[13] W.T. Read. *Dislocations in Crystals*, McGraw-Hill, New York (Section 8.4) (1953).
[14] J.M. Kosterlitz, D.J. Thouless. *J. Phys. C*, **5**, L124 (1972) and **6**, 1181 (1973).