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Interfacial layer effect on specific heat of colloidal suspensions

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Abstract

A theoretical model for the specific heat of nanofluids containing oxide based nanoparticles of different sizes and at different temperatures has been presented. The model proposed by Xuan and Roetzel has been modified by incorporating the effect of semi-solid interfacial layer, which is formed due to adsorption of base fluid molecules on the surface of nanoparticles. The contribution of this layer has been taken into account by assuming that the heat capacity as well as the density of interfacial layer lies between the corresponding values for the nanoparticle and the fluid and as such these have been estimated by taking the arithmetic and the geometric means of the relevant quantities. It is observed that the specific heat capacity of the nanofluid decreases with increase in particle volume fraction and that the presence of interfacial layer enhances the value even though its thickness has been taken to be only 1-2 nm as estimated by Xue *et al.* using molecular dynamics simulation. The effects of interfacial layer thickness, nanoparticle size, volume fraction, and specific heat ratio of particle to fluid have been discussed. The obtained results are in good agreement with some recent available experimental data. Copyright © 2017 VBRI Press.

Keywords: Nanofluids, specific heat, interfacial layer.

Introduction

Stable colloidal suspensions of nanoparticles in base fluids, termed as nanofluids, have attracted the attention of researchers as well as industries because of their numerous potential applications [**1**, **2**]. Specific heat is an important thermo physical property like thermal conductivity, viscosity, and diffusivity of nanofluids, which needs being explored further to make their applications more pertinent to cooling processes, transportation and microelectronics. It is reported in the literature that specific heat of nanofluids is higher than that of the base fluid and that it decreases with increase in particle volume fraction and temperature. Wang *et al.* [**3**] proposed a theoretical model employing the concept of elastic continuum and demonstrated the effect of temperature, size and the softening of surface atom vibrations on Copper oxide nanoparticles. Enhancement in specific heat capacity was attributed to the quantum effects.

Numerous experimental techniques have been employed to investigate the specific heat of Nanofluid systems. One of the popular approach is by employing Differential Scanning Calorimeter technique [**4**, **5**]. A recent report demonstrates the increased specific heat of nanofluids based on molten salts, nitrate salt-alumina nanoparticles which find potential applications in solar thermal energy systems [**6**]. Quasi isothermal temperature modulated differential scanning calorimeter technique has also been employed [**7**] in the temperature range from 243.15 to 473.15 K. Flow loop experiments has also been carried out [**8**] by using polyalphaolefin nanofluids. An anomalous enhancement was also observed in alkali metal chloride doped with silica nanoparticles which was ascribed to increased specific heat of nanoparticles, solid-fluid interaction and layering of liquid molecules at the surface of nanoparticles [**9**, **10**]. An experimental investigation has also been carried out [**11**] on the thermo-physical properties and overall performance of MWCNT/heat transfer oil nanofluids flow inside vertical helically coiled tubes. A generalized regression equation [**12**] has also been put forth to analyze the variations observed in the specific heat because of thermal diffusivity. Molecular Dynamics modeling [**13**] has also been reported for these systems. Elias *et al.* [**14**] have reported trends for Radiator Coolant (RC) based nanofluids. Ultra violet-visible (UV-Vis) absorption and Fourier transform infrared (FTIR) spectroscopies were coupled with thermogravimetric analysis [**15**] to obtain dodecylbenzenesulfonic acid doped polyaniline (DBSA-doped PANI). Recently, experiments were carried out by employing differential thermal analysis technique [**16**].

However, none of the researchers report well defined mechanisms responsible for the trend observed for specific heat of nanofluids. Therefore, in the present theoretical work, we have presented an analysis which incorporates the effect of the interfacial layer formed around the nanoparticles to explain various aspects of the behavior of specific heat of nanofluids. This work may possibly contribute to the development of effective thermal energy storage systems. This may enable a significant reduction in the monetary value of heat recovery systems which are mostly struggling to master the present challenging issues such as climate change, global heating, and greenhouse effect.

Theoretical modelling

In this section, we considered an interfacial nanolayer with linear specific heat distribution and attempted to deduce an expression for calculating the specific heat of nanofluid, which includes the impact of nanolayer. The effects of nanolayer thickness, volume fraction, nanoparticle size, and specific heat ratio of particle to fluid have been discussed.

Interfacial layer

There is formation of semi-solid like layer of fluid molecules around the surface of nanoparticles, termed as ‘interfacial layer’ which exhibits different physicochemical properties than that of nanoparticles and bulk fluid. The thermophysical properties and thickness of this layer has functional dependence on suspended nanoparticles, base fluid and interactions among them which make the heat transfer across the solid-liquid interface effective. Therefore, the behavior of this interfacial layer needs to be investigated thoroughly based on various fluid parameters. Although there is no available expression for calculating the specific heat of the interfacial layer, it is expected to have intermediate specific heat between that of bulk fluid (c_f) and nanoparticle (c_p). In order to study the role of interfacial layer, consider a nanofluid consisting of spherical nanoparticles of radius r_p and the concentration of particles, ϕ. After dispersion of nanoparticles, there is a gradual formation of nanolayer of thickness *h* which is more ordered than that of bulk fluid. Following the same methodology as that for distribution of thermal conductivity [**17**] inside the nanolayer, an analysis for specific heat has been carried out. Let us consider the distribution of heat transfer within the layer as given by:

$$S_l = \int_{r_p}^{r_p+h} \frac{dr}{4\pi r^2 C(r)}. \qquad (1)$$

Also, it can be expressed as average heat of nanolayer the, c_{layer}, as

$$S_l = \frac{1}{4\pi c_{layer}}\left(\frac{1}{r_p} - \frac{1}{r_p+h}\right) \qquad (2)$$

From Eqns. (1) and (2), we get

$$c_{layer} = \frac{h}{r_p(r_p+h)\int_{r_p}^{r_p+h} \frac{dr}{r^2 C(r)}}. \qquad (3)$$

Here, C(r) involves physiochemical interactions inside the suspension. In order to reduce the mathematical complexity, we assume linear variation of C(r) as below

$$C(r) = \frac{c_f - c_p}{h} r + \frac{c_p(r_p+h) - c_f r_p}{h}. \qquad (4)$$

Using Eqns. (3) and (4), we obtain specific heat of interfacial layer as

$$c_{layer} = \frac{c_f L^2}{(L-\delta)\ln(1+L)+\delta L}. \qquad (5)$$

where, $L = \varepsilon_p(1+\delta) - 1$ with $\varepsilon_p = c_p/c_f$ as the dimensionless specific heat of nanoparticles and $\delta = h/r_p$ is the ratio of interfacial layer thickness to particle radius. Equation 5 shows that specific heat is a function of reduced specific heat of nanoparticles, nanolayer thickness, particle radius and specific heat of nanoparticles and base fluid. The variation in specific heat ratio c_{layer}/c_f as a function of particle size has been shown in **Fig. 1**.

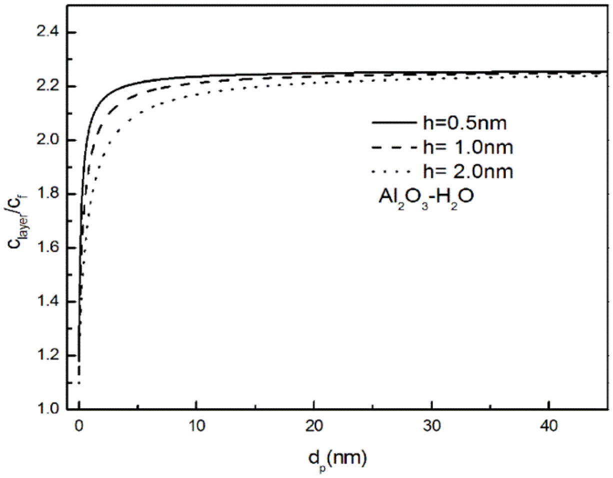

Fig. 1. Specific heat ratio of interfacial layer as a function of particle size d_p.

Another approach to calculate the specific heat of interfacial layer is guided by the fact that the interfacial layer has thermo physical properties intermediate between the solid nanoparticle and the base fluid, we define specific heat and density of this layer by taking the arithmetic and geometric means so that:

$$c_{layer} = \frac{c_f + c_p}{2}, \text{ Or } c_{layer} = \sqrt{c_f c_p} \qquad (6)$$

and

$$\rho_{layer} = \frac{\rho_f + \rho_p}{2}, \text{ Or } \quad \rho_{layer} = \sqrt{\rho_f \rho_p} \tag{7}$$

However, when the calculations were executed, no significant difference was observed in the results with the two approaches. Accordingly, the results being presented here has been analyzed using only the arithmetic means.
In the next section, contribution of interfacial layer to the specific heat of nanofluids has been discussed in detail.

Specific heat of nanofluids

Specific heat can be computed from heat flow measurements and differential temperature through

$$\Delta Q = mc\Delta T \tag{8}$$

where, ΔQ is the heat supplied to the mass m of the substance, c is the specific heat and ΔT is the concerned temperature range.

The density of nanofluids, $\rho_{nf,}$ is described by the physical mixture rule as

$$\rho_{nf} = (1-\phi)\rho_f + \phi\rho_p. \tag{9}$$

Here ρ_f, and ρ_p are the densities of base fluid and the nanoparticles, respectively. Exploiting this rule, following two models have been extensively applied for experimental and numerical investigations at constant pressure specific heat, C_p.

Model I: The first equation used was based on the weighting of the components in the nanofluid analogous to mixing theory for ideal gases by Pak and Cho [**18**]:

$$c_{p,nf} = \phi c_{p,p} + (1-\phi)c_{p,f} \tag{10}$$

This model has been used to study the heat transfer performance of nanofluids in experimental investigations [**19**] and for simulations [**20**].

Model II: This model, proposed by Xuan and Roetzel [**24**], is based on the assumption that there exists a thermal equilibrium between the nanoparticle and base fluid and the expression reads

$$c_{p,nf} = \frac{(1-\phi)(\rho c_p)_f + \phi(\rho c_p)_p}{\phi\rho_p + (1-\phi)\rho_f} \tag{11}$$

This involves the parameters of the nanoparticle as well as and base fluid and is similar to the expression used in the study for various transport properties of nanofluids such as thermal conductivity [**22**], thermal diffusivity [**23**] and convection heat transfer [**24**]. The contribution of semi solid layer of fluid particles around the nanoparticle which is called as interfacial layer has been incorporated in model II which we call as model III (M-III) hereafter. It is assumed that the bare particle and the equivalent nanoparticle formed with interfacial layer around it are both spherical with respective radii r_p and r_p+h, where the layer thickness h is quite small as compared to r_p. The effective volume for the latter is given as

$$V_{eq} = V_p + V_{layer} \tag{12}$$

where, $V_p(=4pr_p^3/3)$ and $V_{layer}(= 4pr_p^3 d \text{ with } d = h/r_p)$ are the volumes of the particle and the interfacial layer, respectively. The volume fraction of the equivalent particle can be written as

$$\phi_{eq} = \frac{V_{eq}}{V_t} = \frac{V_p + V_{layer}}{V_t} = \frac{V_p}{V_t} + \frac{V_{layer}}{V_t}, \tag{13}$$

where, V_t is the total volume fraction of particles. Therefore,

$$\phi_{eq} = \phi_p + \phi_{layer}. \tag{14}$$

The effective density of the nanofluid can be written as

$$\rho_{nf} = \rho_f(1-\phi) + (\rho_p V_p + \rho_{layer} V_{layer})\phi \tag{15}$$

Similarly, specific heat capacity is given by

$$(\rho c_p)_{nf} = \phi_p(\rho c_p)_p + \phi_{layer}(\rho c_p)_{layer} + (1-\phi_{eq})(\rho c_p)_f. \tag{16}$$

And this together with Eqn. (8) gives expression for specific heat of nanofluid as

$$(c_p)_{nf} = \frac{\phi_p(\rho c_p)_p + \phi_{layer}(\rho c_p)_{layer} + (1-\phi_{eq})(\rho c_p)_f}{\rho_p\phi_p + \rho_{layer}\phi_{layer} + (1-\phi_{eq})\rho_f}. \tag{17}$$

In our calculations, the results obtained using Eqns. (17) and (5) shall be called as M-III approach-I and using Eqns. (17) and (6) as M-III approach-II.

Results and discussion

In order to calculate the specific heat of nanofluids, Eqn. (17) has been employed along with the involved parameters as listed in **Table 1**. for various nanofluid systems.

Table 1. Parameters used in the calculation of specific heat of nanofluids.

System	Density [gcm^{-3}]	Specific heat [Jg^{-1}K^{-1}]
Al_2O_3-H_2O	ρ_p=3.6 for bulk Al_2O_3 [**26**] ρ_f=0.9947 for water [**27**]	$c_{p,p}$=0.7910 bulk [**26**] and 1.0474 (for 20 nm) at T=306 K [**26**], $c_{p,f}$=4.1707 [**26**]
SiO_2- H_2O	ρ_p =2.22 [**28**] and ρ_f= 0.98573 [**29**]	$c_{p,p}$=0.745 (for 20 nm) [**28**] $c_{p,f}$=4.1824 [**29**]

The specific heat $c_{p,nf}$ of Al_2O_3-H_2O nanofluid system for d_p=45nm as function of equivalent nanoparticle volume fraction ϕ has been shown in **Fig. 2** wherein the results obtained with bulk specific heat of Al_2O_3, specific heat of nanoparticles and Model-II (M-II) have been plotted along with the available experimental data [**4**] for comparison. Works reported so far have calculated the specific heat without using the concept of interfacial layers. In the present work, the thickness of interfacial layer has been chosen to lie within 1 or 2 nm [**25**] and is expected to have heat capacity in between that of nanoparticle and base fluid. It has been observed that experimental data matches more closely with our calculated results M-III approach-I.

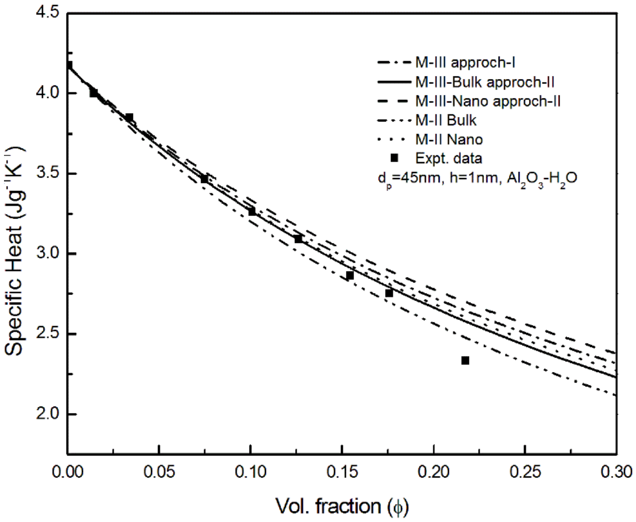

Fig. 2. Variation of specific heat for Al_2O_3-H_2O (d_p=45nm) system with particle volume fraction and comparison with expt. data. [**4**]

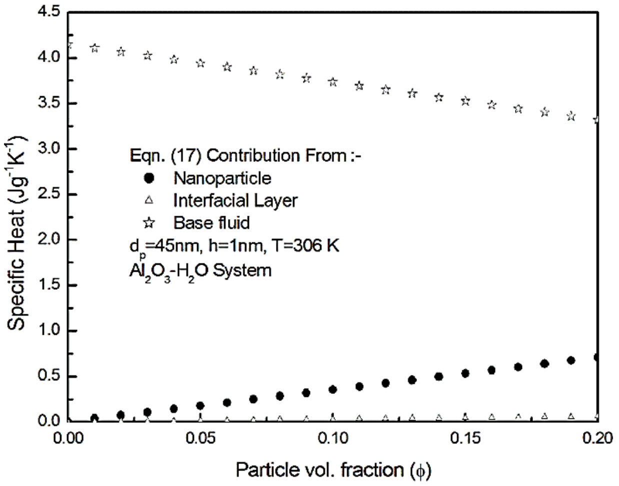

Fig. 3. Contrastive contributions of nanoparticle, interfacial layer and base fluid to specific heat of nanofluid as a function of particle volume fraction.

Fig. 3. has been plotted to bring out separate contributions from nanofluid components as a function of particle volume fraction. It is shown that the contributions of nanoparticles and interfacial layer increase, with increase in the particle concentration although interfacial layer contributes significantly less. The contribution of base fluid is found to decrease with increase in particle volume fraction. This implies that as the fluid has higher specific heat, the overall heat capacity of nanofluids decrease with increase in concentration of nanoparticles.

Plot of silica-water (d_p=32 nm) at temperature 328 K has been depicted in **Fig. 4**. Here, calculated results with M-III approach-I are found to agree well with the experimental data [**30**] as compared to M-III approach-II and M-II supporting the existence of interfacial layer contribution to heat capacity of nanofluid system. Specific heat is an extensive property which depends on the structure of the substance, in particular, the number of degrees available to particles in the substance. Lesser number of internal degrees of freedom tends to decrease the specific heat. So the formation of interfacial layer around the nanoparticles resembles more like solid structure which decreases the specific heat of nanofluids with increase in particle volume fraction.

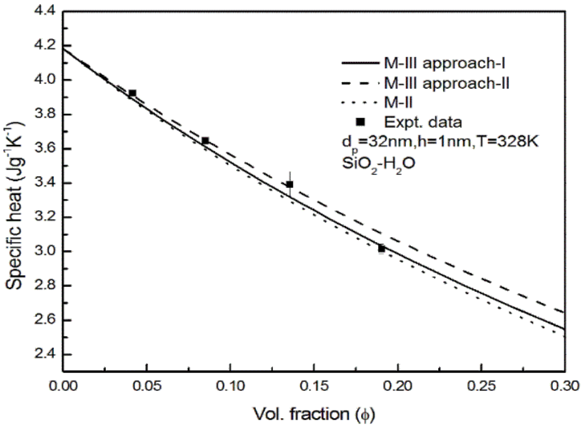

Fig. 4. Specific heat of SiO_2-H_2O with particle volume fraction. Curves solid line (—) represent results for M-III-approach-I. Dash (— —) represents results for M-III approach-II Dot (…) correspond to M-II. And Solid squares represent (▪) correspond to experimental data with error bars [**30**].

Conclusion

In this work, the role and significance of interfacial layer on the specific heat of nanofluids has been brought out. The specific heat of nanofluid decreases almost linearly with increasing volume fraction of nanoparticles. Because of the much smaller specific heat of solid nanoparticles and that of interfacial layer around them which resembles more like compact solid structure as compared to that of liquids, the overall specific heat of nanofluids decreases as the volume fraction increases, there is a corresponding decrease in the heat capacity. The specific heat of nanoparticles rather than bulk of the same material have higher values. The interfacial layer increases the overall volume fraction of the nanoparticles which, in turn, decreases the specific heat of the system.

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References

1. Keblinski, P.; Phillpot, S.R.; Choi, S.U.S., Eastman, J.A. *Int. J. Heat Mass Trans.* **2002**, 45, 855.

DOI: 10.1016/S0017-9310(01)00175-2

2. Taylor,R. A.; Coulombe, S.; Otanicar, T.;Phelan, P.; Gunawan, A.; Lv, W.; Rosengarten, G.; Prasher, R.; Tyagi, H. *J. Appl. Phys.* **2013**, 113, 011301.
   DOI: org/10.1063/1.4754271
3. Wang, B.X.; Zhou, L. P.; Peng, X.F.; *Int. J. Thermophys.* **2006**, 27, 139.
   DOI: 10.1155/2010/172085
4. Zhou, S. Q.; Ni, R.; *Appl. Phys. Lett.* **2008**, 92, 093123.
   DOI: 10.1063/1.2890431
5. Robertis, E. De.; Cosme, E. H. H.; Neves, R. S.; Kuznetsov, A.Y.; Campos, A. P. C.; Landi, S. M.; Achete, C. A.; *Appl. Therm. Eng.* **2012**, 41, 10.
   DOI: 10.1016/j.applthermaleng.2012.01.003
6. Schuller, M. M.; Shao, Q.; Lalk, T. *Int. J. Therm. Sc.* **2015**, 91, 142.
   DOI: 10.1016/j.ijthermalsci.2015.01.012
7. Cabaleiro, D.; Gracia-Fernández, C.; Legido, J.L.; Lugo, L.; *Int J Heat Mass Trans.* **2015**, 88,872.
   DOI: 10.1016/j.ijheatmasstransfer.2015.04.107
8. Nelson, I. C.; Banerjee, D.; Ponnappan, R.; J. *Thermophys Heat Trans* .**2009**, 23, 752
   DOI: 10.2514/1.31033
9. Shin D.; Banerjee, D.; *Int. J. Heat and Mass Trans.* **2011**, 54, 1064.
   DOI: 10.1016/j.ijheatmasstransfer.2010.11.017
10. Prasher, R.; Bhattacharya, P.; Phelan, P.E.; *ASME J. Heat Trans.***2006**, 128, 588
    DOI: 10.1115/1.2188509
11. Pakdaman, F. M.; Akhavan-Behabadi, M.A.; Razi, P;.*Exp Therm Fluid Sci.***2012**, 40, 103–11.
    DOI: 10.1016/j.expthermflusci.2012.02.005
12. Sekhar, Y.R.; Sharma, K.V.; *J Exp Nanosci.* **2013**, 10, 86.
    DOI: 10.1080/17458080.2013.796595
13. Rajabpour, A.; Akizi, F. Y.; Heyhat, M. M.; Gordiz, K.; *Int. Nano Lett.* **2013**, 3, 1.
    DOI: 10.1186/2228-5326-3-58
14. Elias, M. M.; Mahbubul, I. M.; Saidur, R.;Sohel, M. R.; Shahrul, I. M.; Khaleduzzaman, S.S.; Sadeghipour, S.; *Int Commun Heat Mass Trans*. **2014**, 54, 48.
    DOI: 10.1016/j.icheatmasstransfer.2014.03.005
15. Chew, T. S.; Rusli, D.; Muhammad, A. A. H.; *Polymers* **2015**, *7*, 1221.
    DOI: 10.3390/polym7071221
16. Yiamsawasd, T.; Dalkilic, A. S.; Wongwises, S.; **2016**, 8, 939.
    DOI: 10.2174/157341312803989132
17. Xie, H.; Fujii, M.; Zhang, X. *Int. J. Heat Mass Trans.* **2005**, 48, 2926.
    DOI: 10.1016/j.ijheatmasstransfer.2004.10.040
18. Pak, B. C.; Cho, Y.; *Exp. Heat Trans.* **1998,** 11, 151.
    DOI: 10.1080/08916159808946559
19. Lee, J.; Mudawar, I.; *Int. J. Heat Mass Trans.***2007**, 50, 452.
    DOI: 10.1016/j.ijheatmasstransfer.2006.08.001
20. Polidori, G.; Fohanno, S.; Nguyen, C. T.; *Int. J. Therm. Sci*. **2007**, 46, 739.
    DOI: 10.1016/j.ijthermalsci.2006.11.009
21. Xuan, Y.; Roetzel, W.; *Int. J. Heat and Mass Trans.***2000**, 43, 3701.
    DOI: 10.1016/S0017-9310(99)00369-5
22. Kim, J.; Kang, Y. T.; Choi, C. K.; *Int. J. Refrig.***2007**, 30, 323.
    DOI: 10.1016/j.ijrefrig.2006.04.005
23. Venerus, D. C.; Kabadi, M. S.; Lee, S.; Perez-Luna, V.; *J. Appl. Phys.* **2006**, 100, 094310
    DOI: 10.1063/1.2360378.
24. Nnanna, A. G. A.; *Int. J. Heat Trans*. **2007**, 129, 697.
    DOI: 10.1115/1.2717239
25. Xue, L.; Keblinski, P.; Phillpot, S. R.; Choi, S.U.S.; Eastman, J.A. *Int. Heat Mass Trans* 2004, **47**, 4277.
26. Wang, L.; Tan, Z. C.; Meng, S. H.; Liang, D. B.; Li, G. H. ; J. *Nanopart. Res.***2001**, 3, 483.
    DOI: 10.1186/1556-276X-8-448.
27. Lide, D. R.; Handbook of Chemistry and Physics 74th ed., edited by Chemical Rubber Co., Boca Raton, 1993.
    ISBN: 0-8493-0474-1
28. Vajjha R. S.; Das, D. K.; *Int.J. of Heat Trans.***2009**, 131, 071601-1
    DOI:10.1115/1.3090813.
29. Wallace, K. G.; Research in Heat Transfer with Nanofluids, (Thesis Purdue University **2010**).
30. Hanley, H.O.; Buongiorno, J.; McKrelland, T.; Hu, L. W.; *Advances in Mech. Eng*. **2012**, Article ID 181079.
    DOI:10.1155/2012/181079