

# Adequacy of the Classical Potentials for the study of Thermodynamic Properties of Transition Metal Clusters

Zacharias G. Fthenakis<sup>1,2</sup>, Antonis N. Andriotis<sup>1</sup>

fthenak@iesl.forth.gr

<sup>1</sup>Institute of Electronic Structure and Laser - FORTH

<sup>2</sup>Department of Physics, University of Crete

# Σκοπός

Υπολογισμός μαγνητικών, δομικών και θερμοδυναμικών ιδιοτήτων *clusters* ατόμων μεταβατικών μετάλλων υπό την επίδραση θερμοκρασίας

- Μοριακή Δυναμική **Nose - Hoover**  
(S.Nose, Mol.Phys. **52**, 255, (1984); J.Chem.Phys. **81**, 51, (1984)  
W.G.Hoover, Phys.Rev.A, **31**, 1965, (1985) )
- Προσέγγιση Ισχυρής Δέσμευσης (**Tight Binding**)  
- Σχήμα **Harrisson**
- Ενσωμάτωση όρου **Hubbard**

Όμως ...

Διαγωνοποίηση  $\implies$  Χρόνος  $\sim N^3$

Για  $Ni_{13}$  με Pentium 4 στα 2.53 GHz  
 $\implies \sim 16 - 18$  ώρες για κάθε θερμοκρασία

Z.G.Fthenakis, A.N.Andriotis, M.Menon,  
*Temperature evolution of structural and magnetic  
properties of transition metal clusters,*  
Journal of Chemical Physics

Για cluster 130 ατόμων  $\implies \sim 16 \times 10^3$  ώρες  $\sim$   
2 χρόνια !!!

ΑΠΑΓΟΡΕΥΤΙΚΟ

# Παρά όλα αυτά ...

Κλασικά Δυναμικά  $\implies$

- Όχι διαγωνοποίηση
- Χρόνος  $\sim N^2$  ή και λιγότερο ( $Ni_{13} \longrightarrow 5$  λεπτά)

Νέος Στόχος

- Εύρεση κλασικού δυναμικού που αποδίδει τις ίδιες δομές με την TBH καθώς αλλάζει η θερμοκρασία
- Μοριακή δυναμική με αυτό το δυναμικό
- Υπολογισμός μαγνητικής ροπής από την TBH σε διακεκριμένα βήματα

# Η Μέθοδος

Μοριακή Δυναμική υπό σταθερή θερμοκρασία



Κανονική Κατανομή



Εξισώσεις Nose - Hoover

$$m \frac{d^2 \mathbf{r}_i}{dt^2} = -\nabla_i V - \zeta m \frac{d\mathbf{r}_i}{dt}, \quad i = 1, 2, \dots, N$$

$$Q \frac{d\zeta}{dt} = \sum_i \frac{1}{2} m v_i^2 - \frac{f}{2} k_B T, \quad f = 3N - 6$$

Επίλυση

Στατιστική

MHM

# Θερμοδυναμικές Ποσότητες

## ● Απο ΜΜΗ

- Εντροπία  $S(E) = k_B \ln \Delta\Gamma_i$
- Συνάρτηση Επιμερισμού  $Z(T) = \sum_{E_i} \Delta\Gamma(E_i) e^{-\beta E_i}$
- Εσωτερική Ενέργεια  $U(T) = \frac{\sum_{E_i} \Delta\Gamma(E_i) E_i e^{-\beta E_i}}{Z(T)}$
- Ελεύθερη Ενέργεια  $F(T) = -k_B T \ln Z(T)$
- Ειδική Θερμότητα  $C_V = \frac{\partial U}{\partial T} = \frac{\langle E^2 \rangle - \langle E \rangle^2}{k_B T^2}$

## ● Απο χρονικούς Μέσους Όρους

- Lindemann Index  $\delta = \frac{2}{N(N-1)} \sum_{i < j} \frac{\sqrt{\langle r_{ij}^2 \rangle - \langle r_{ij} \rangle^2}}{\langle r_{ij} \rangle}$
- Μαγνητική Ροπή  $\mu = \frac{1}{N} \sum_i (s_i^{up} - s_i^{down})$

# Επιλογή Δυναμικού

- Κλασσικά Δυναμικά

- Lennard - Jones
- Morse
- Erkoç I
- Cleri - Rosato
- Sutton - Chen
- Erkoç II, Erkoç III
- Uppenbrink - Wales
- EAM (Johnson, ...)

Annual Reviews of Computational Physics IX - edited by  
Dietrich Stauffer - World Scientific - 2001

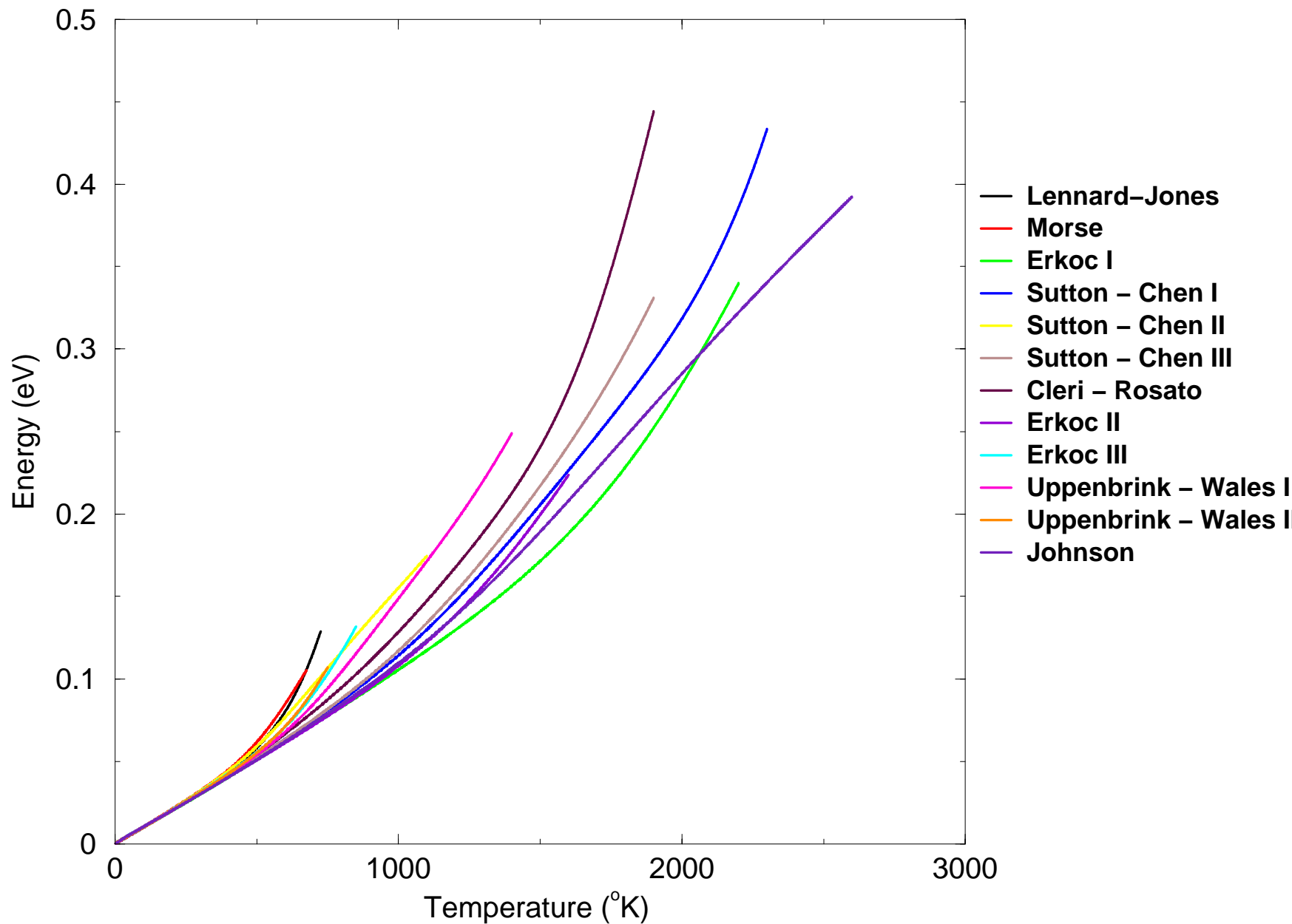
S. Erkoç - *Empirical Potential Energy Functions Used in the  
Simulations of Material Properties*

- Tight Binding Hamiltonian

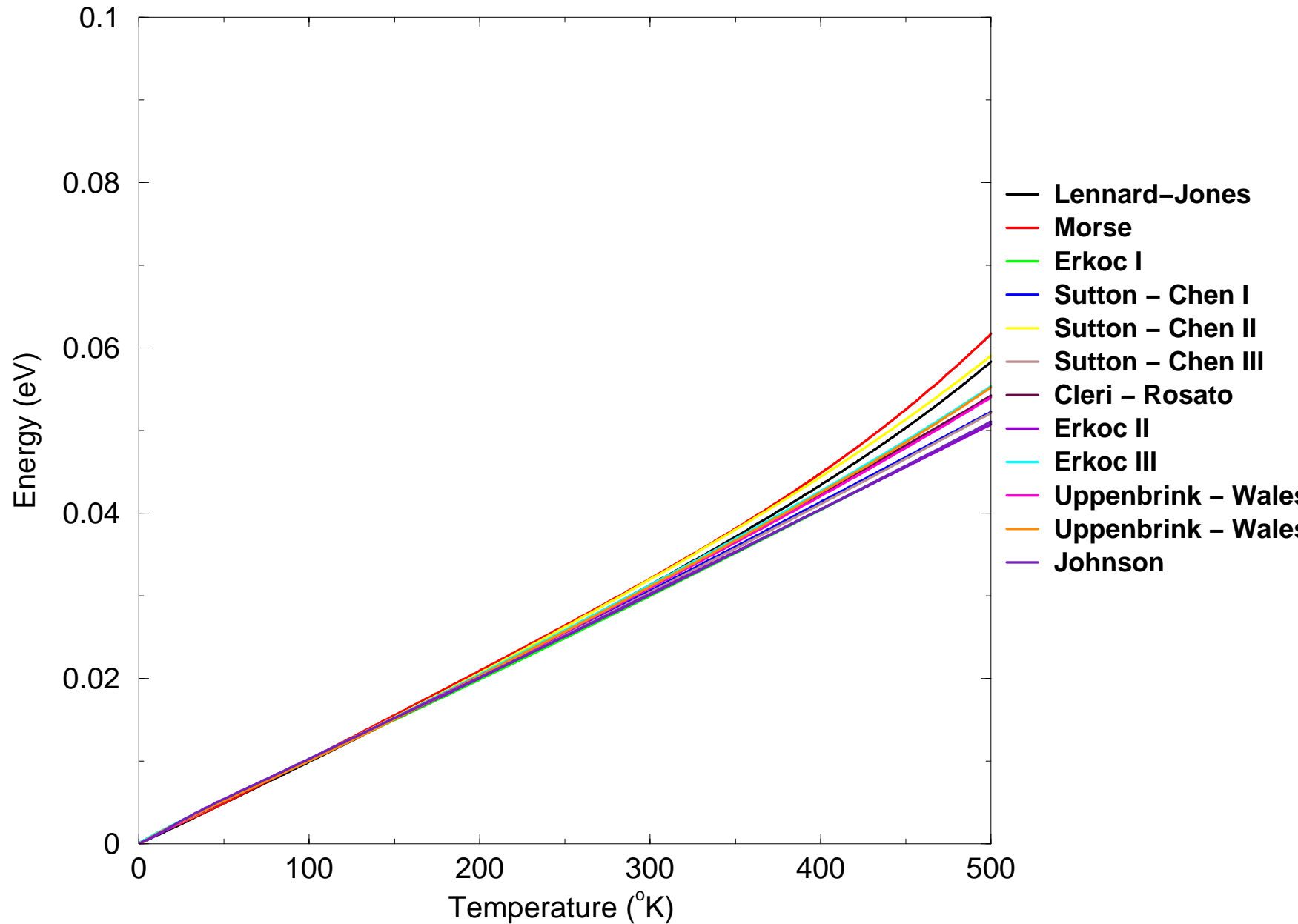
# ΑΠΟΤΕΛΕΣΜΑΤΑ



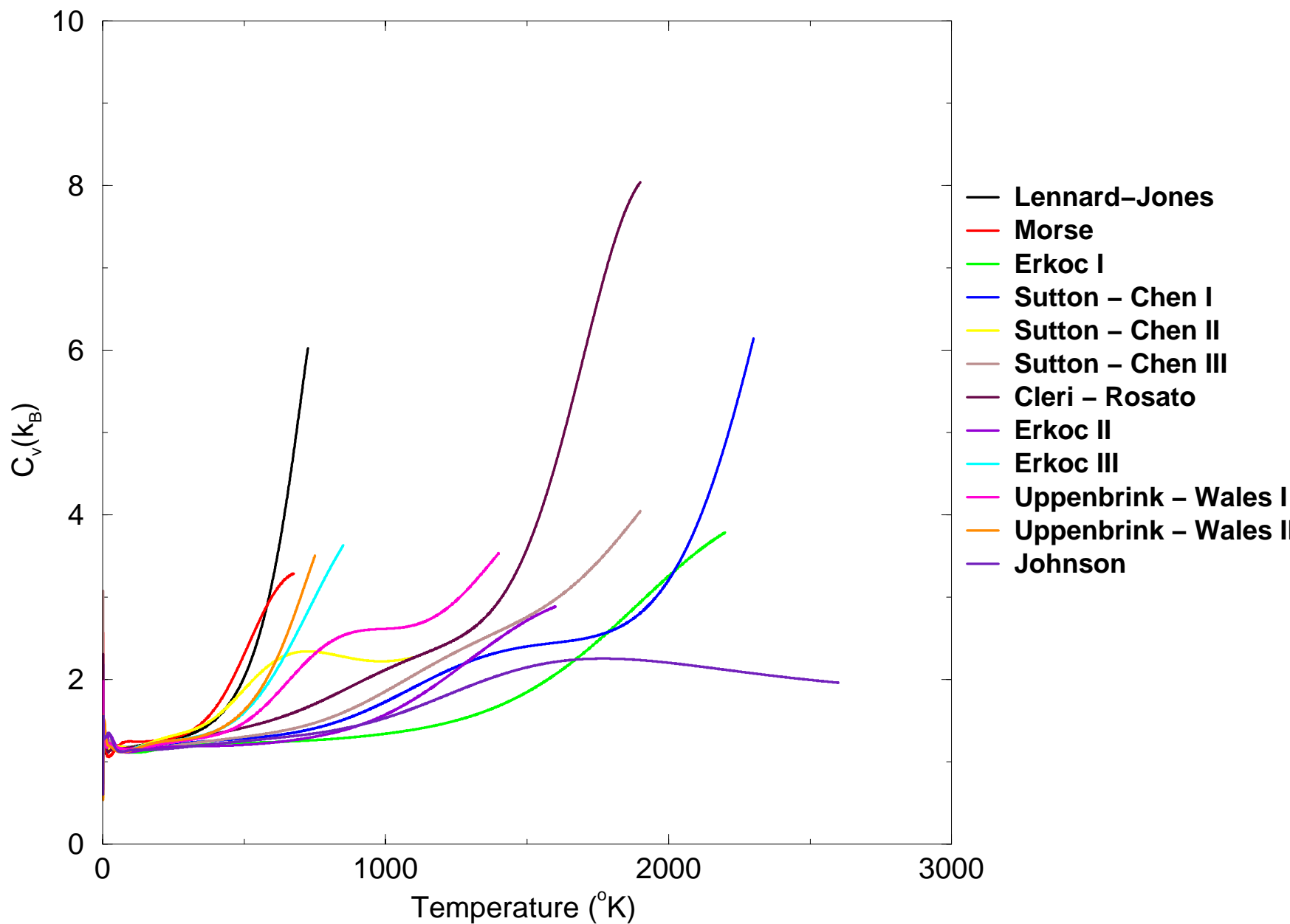
# Energy per atom for the Ni<sub>3</sub> cluster



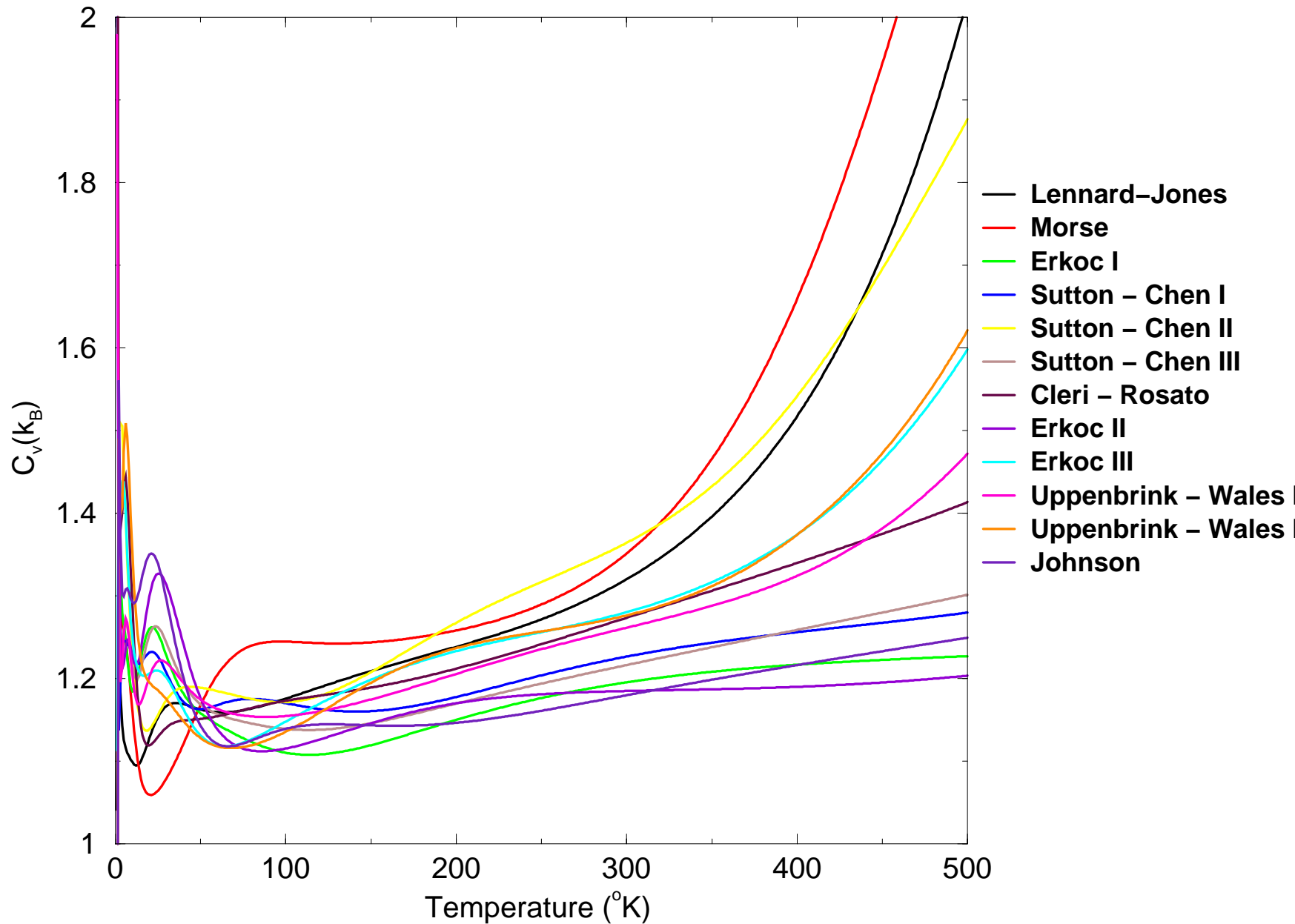
# Energy per atom for the Ni<sub>3</sub> cluster



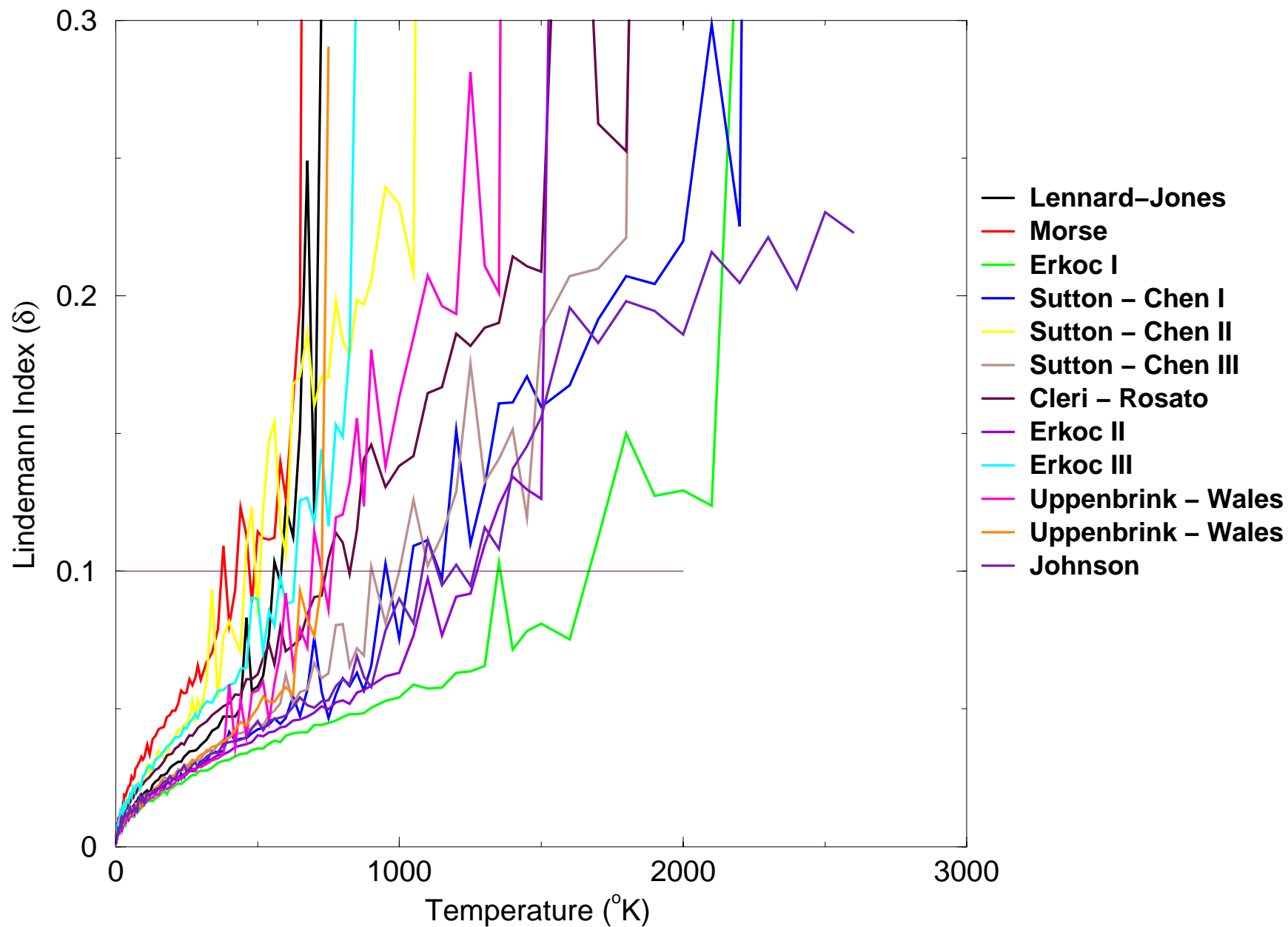
# $C_v$ per atom for the $Ni_3$ cluster



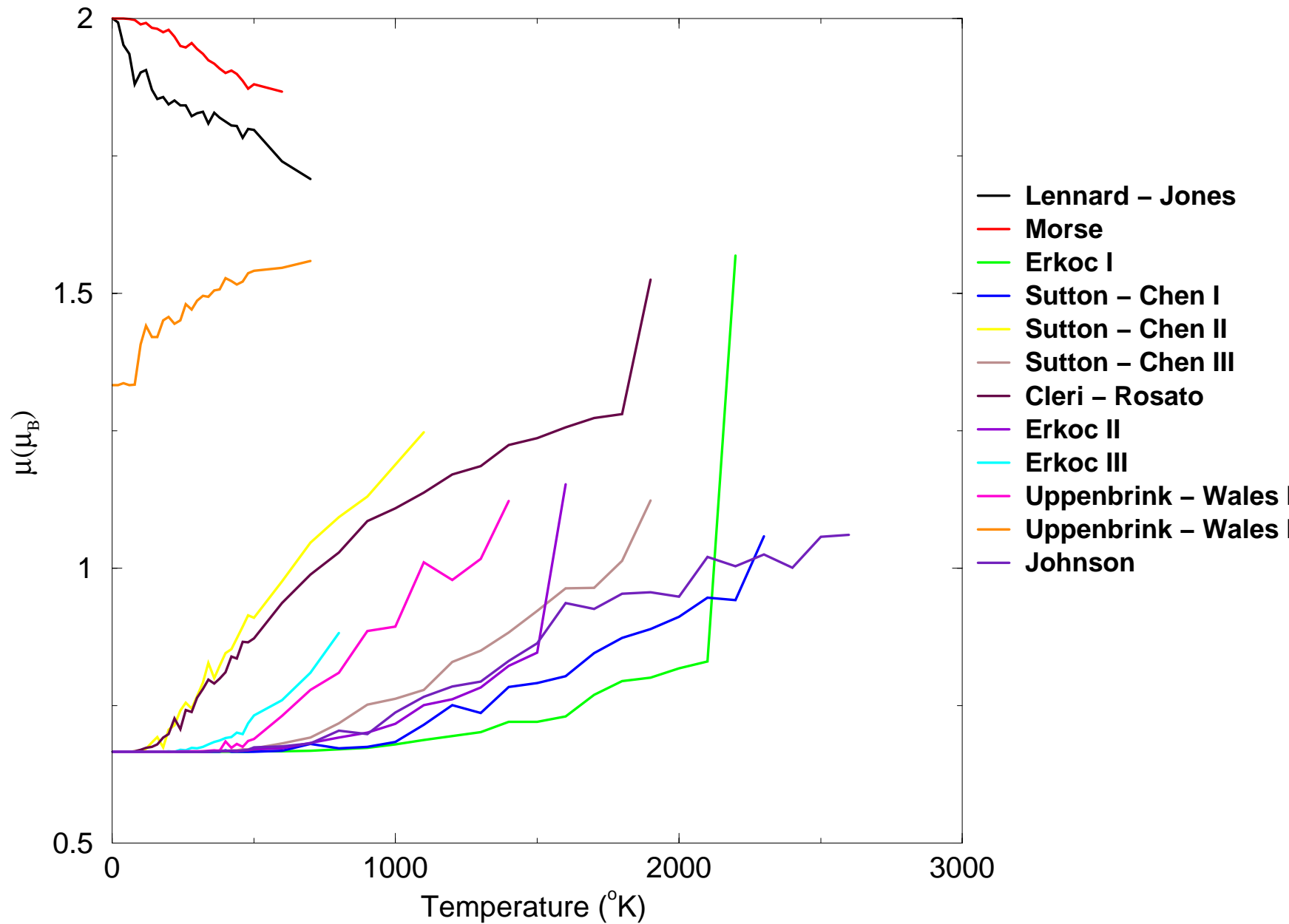
# $C_v$ per atom for the $Ni_3$ cluster



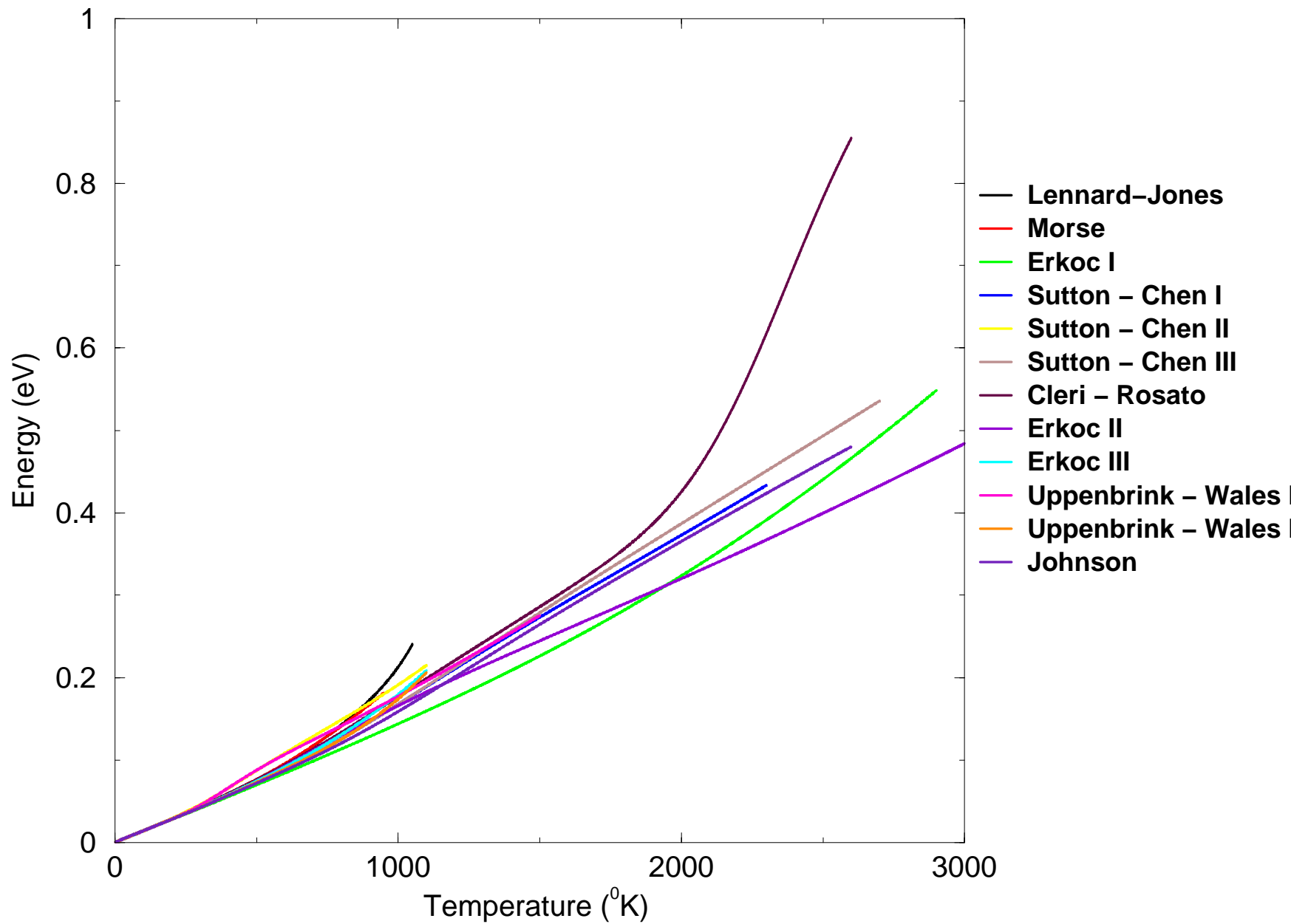
# Lindemann Index for the Ni<sub>3</sub> cluster



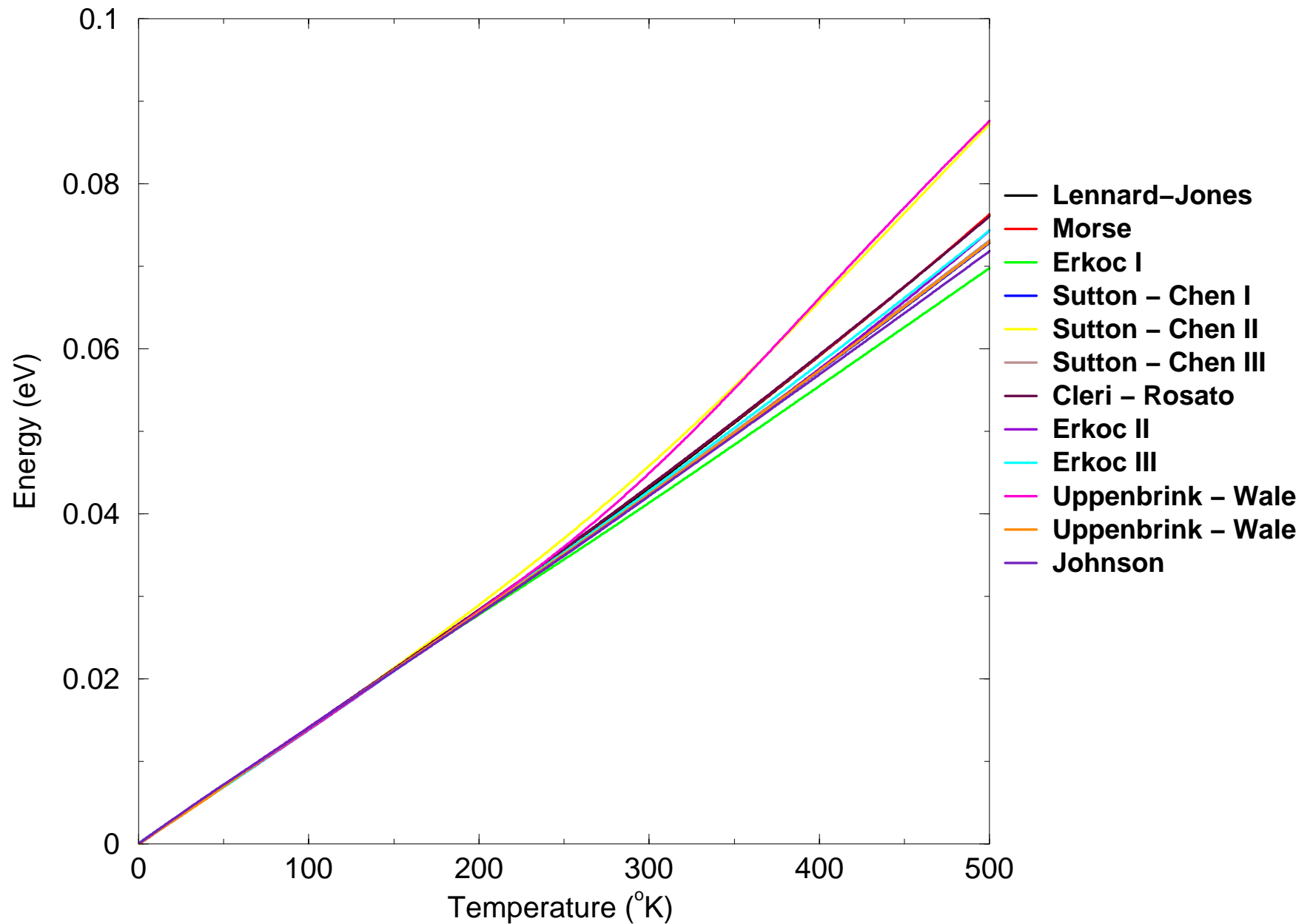
# Magnetic moment per atom for the Ni<sub>3</sub> cluster



# Energy per atom for the Ni<sub>4</sub> cluster

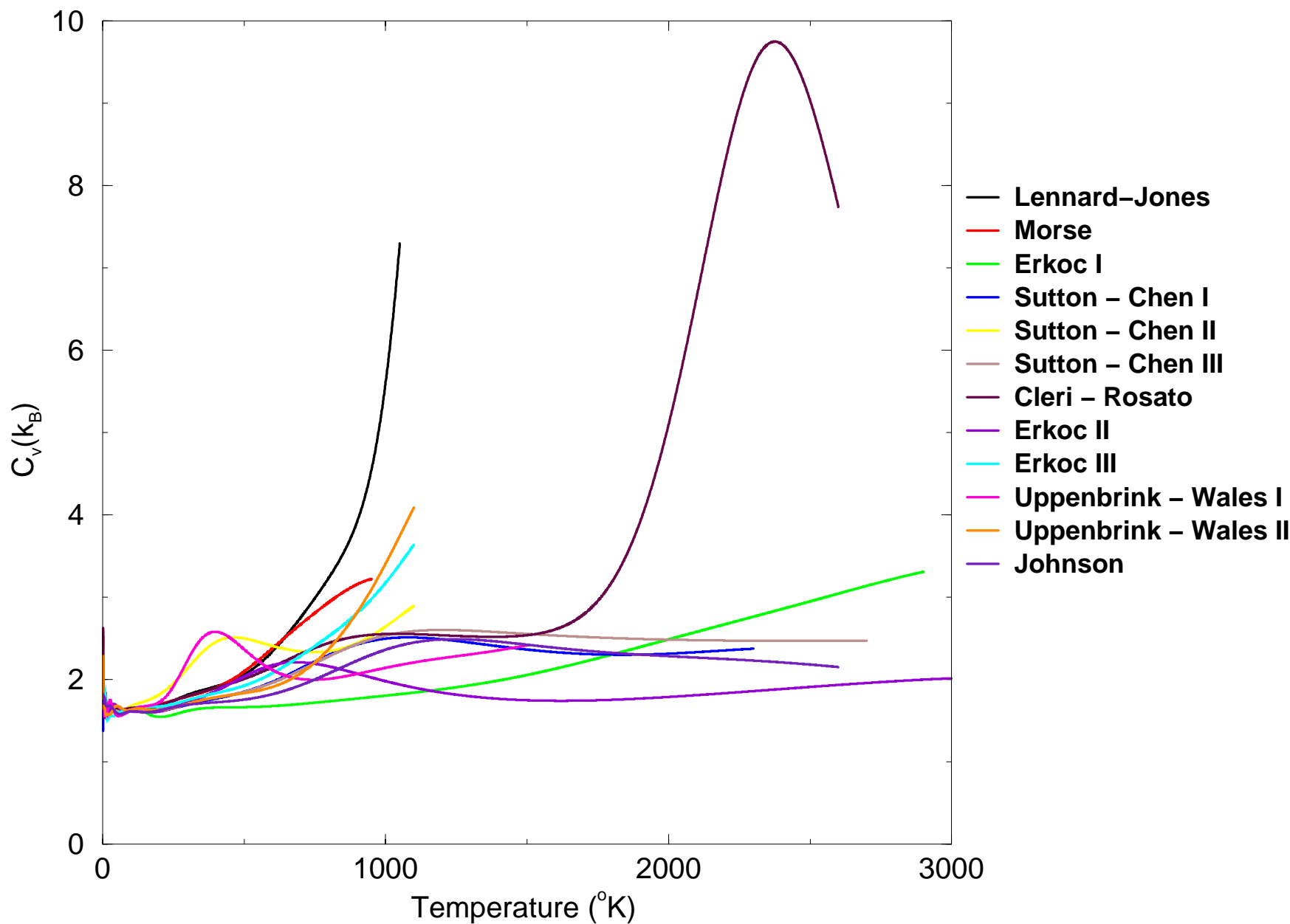


# Energy per atom for the Ni<sub>4</sub> cluster

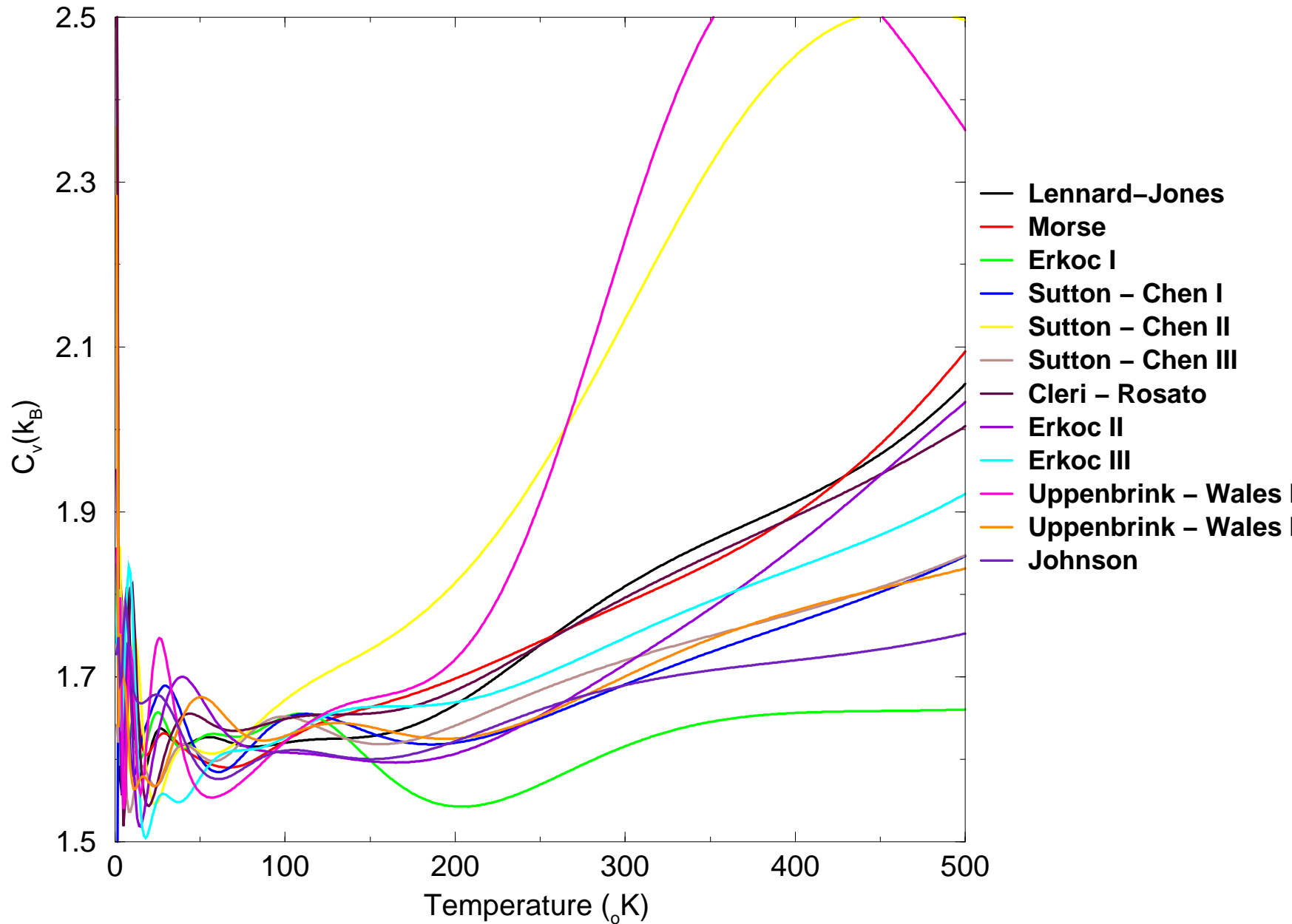




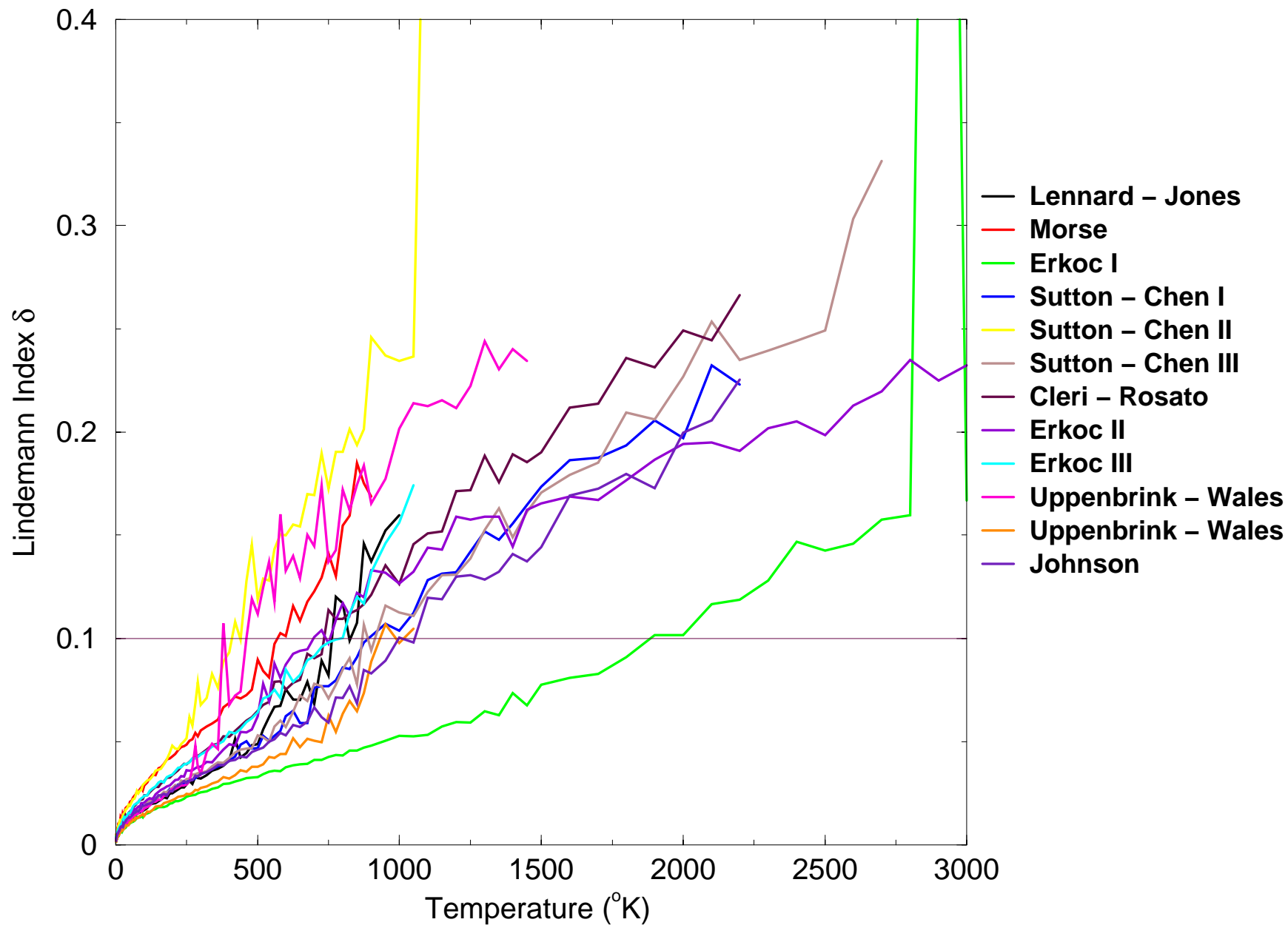
# $C_v$ per atom for the $Ni_4$ cluster



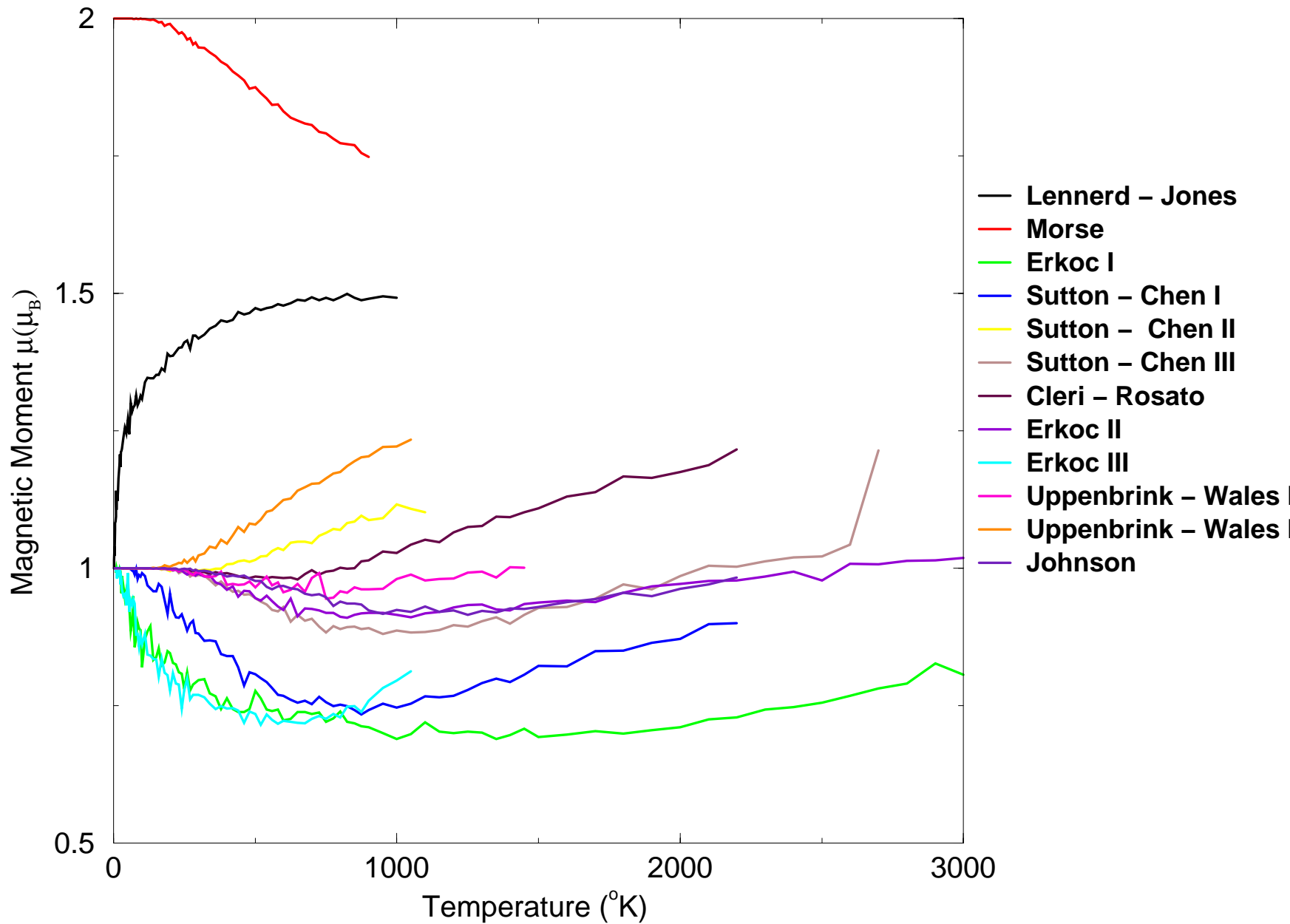
# $C_v$ per atom for the $Ni_4$ cluster



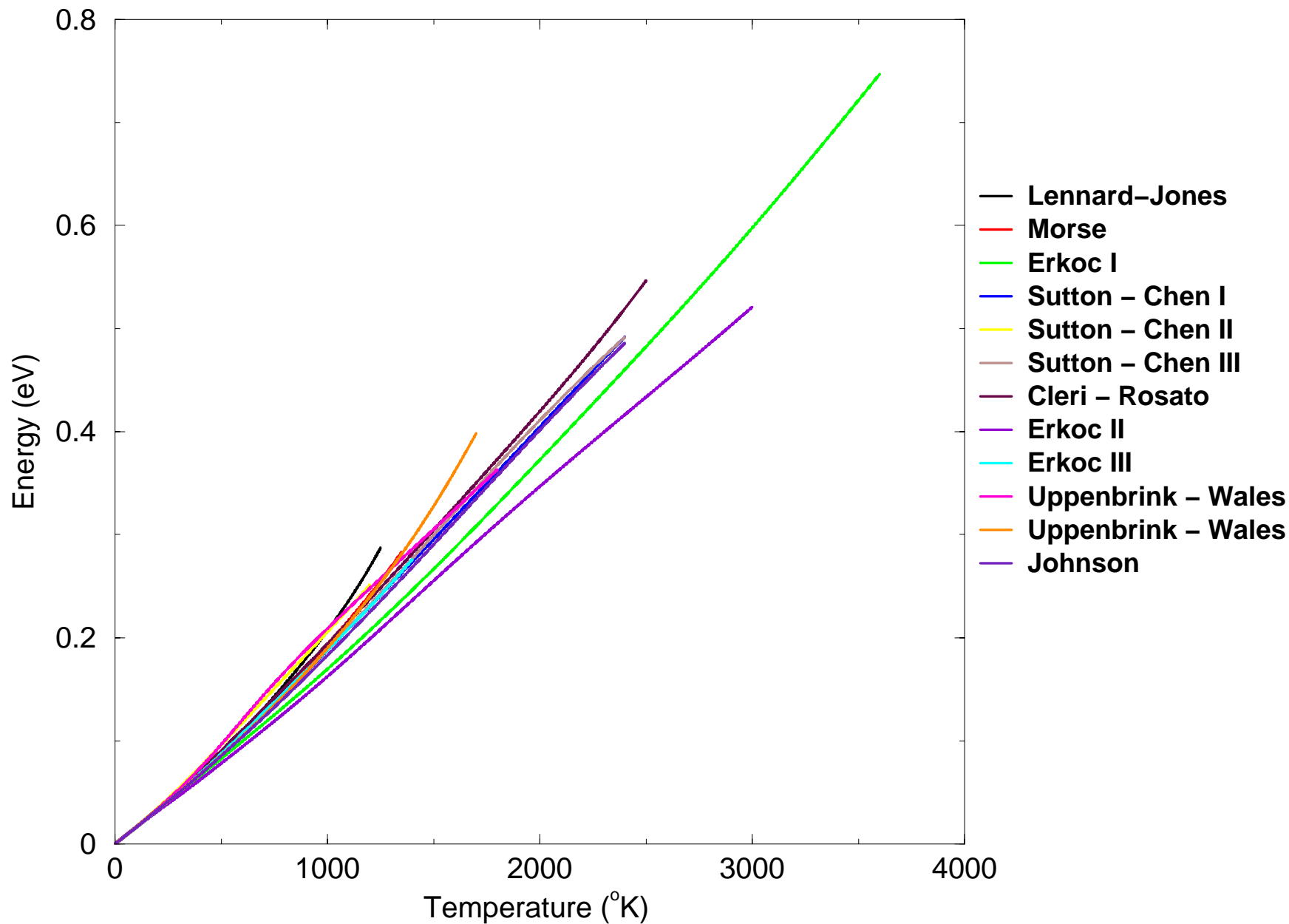
# Lindemann Index for the Ni<sub>4</sub> cluster



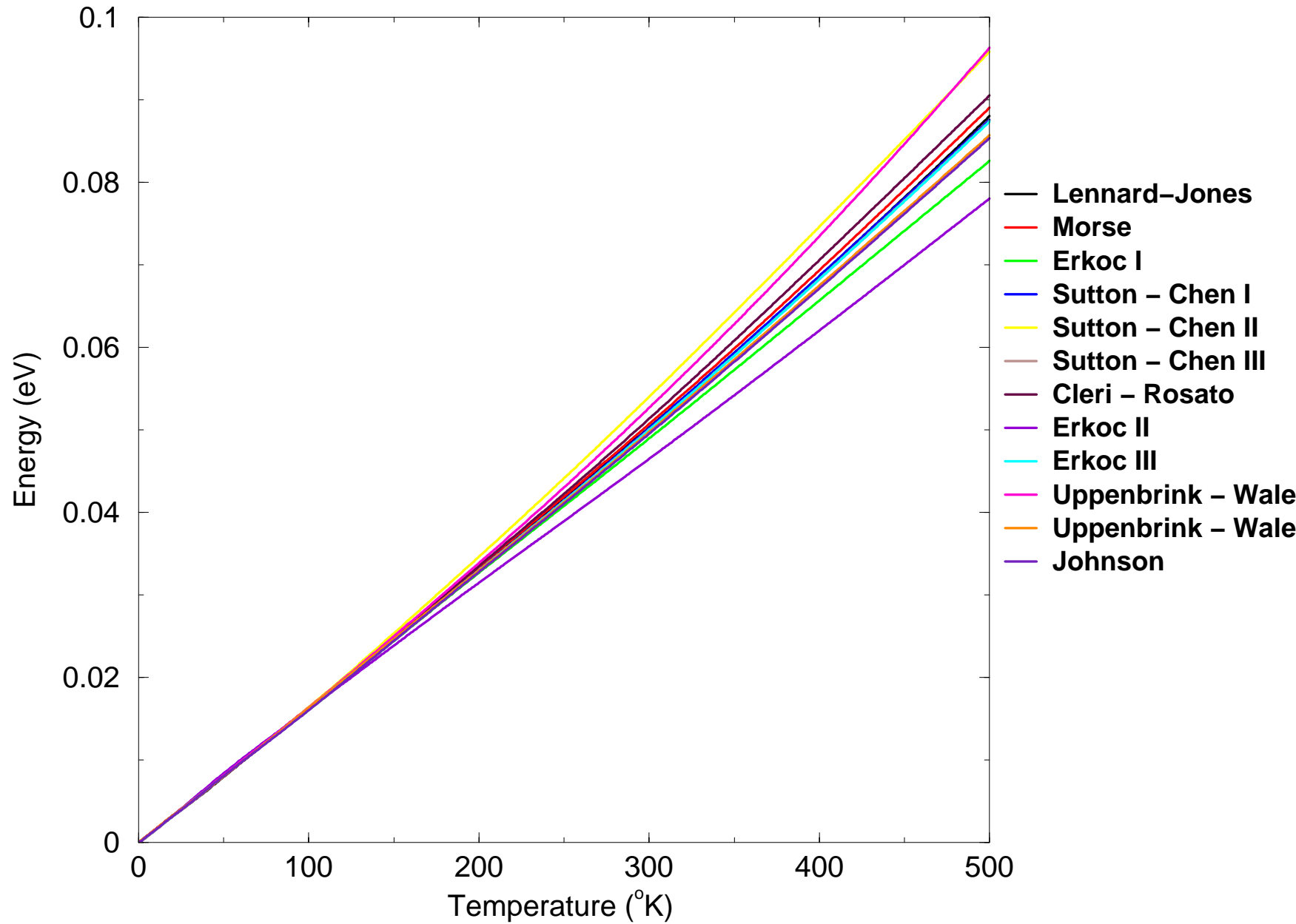
# Magnetic Moment per atom for the Ni<sub>4</sub> cluster



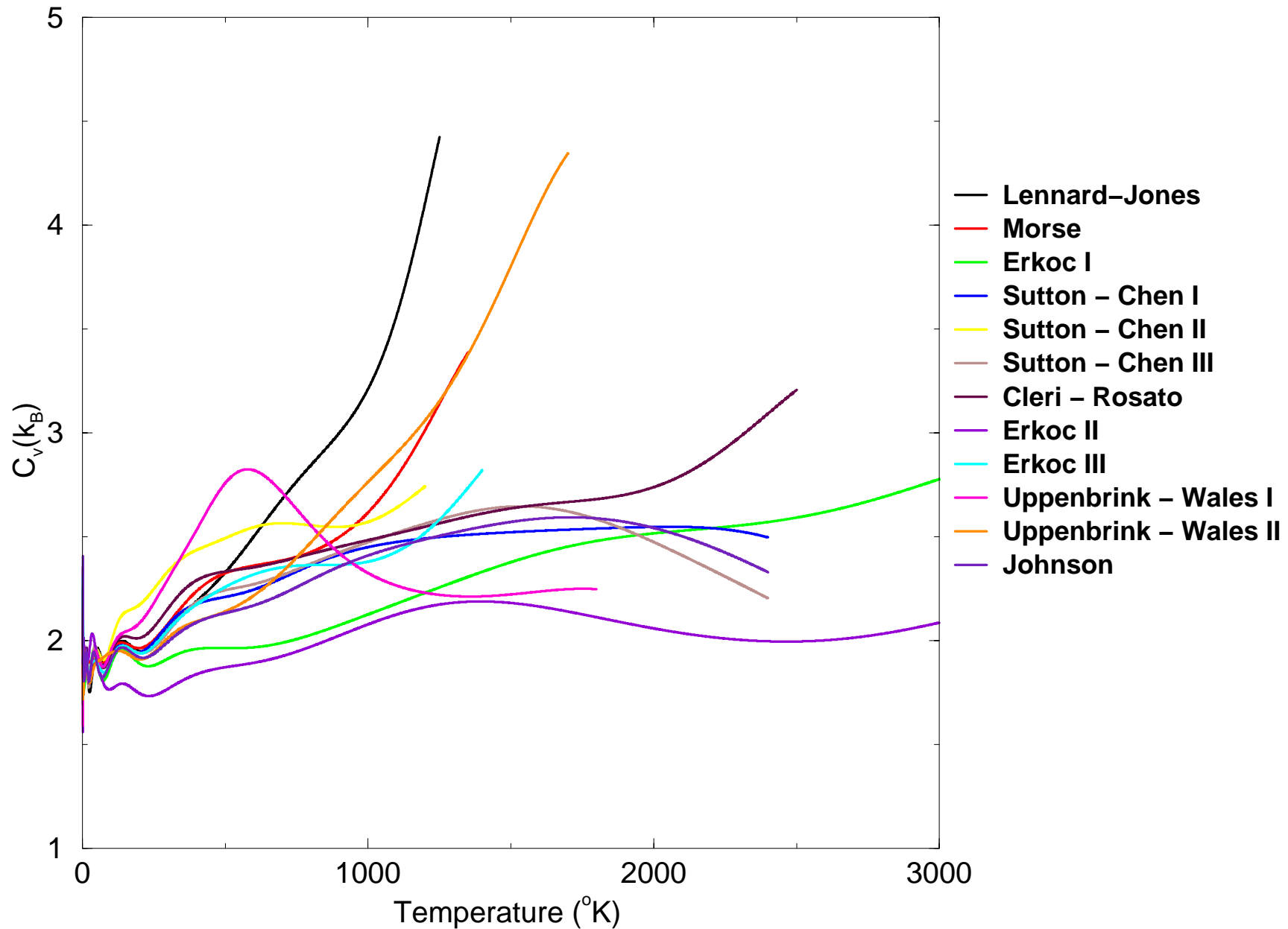
# Energy per atom for the Ni<sub>5</sub> cluster



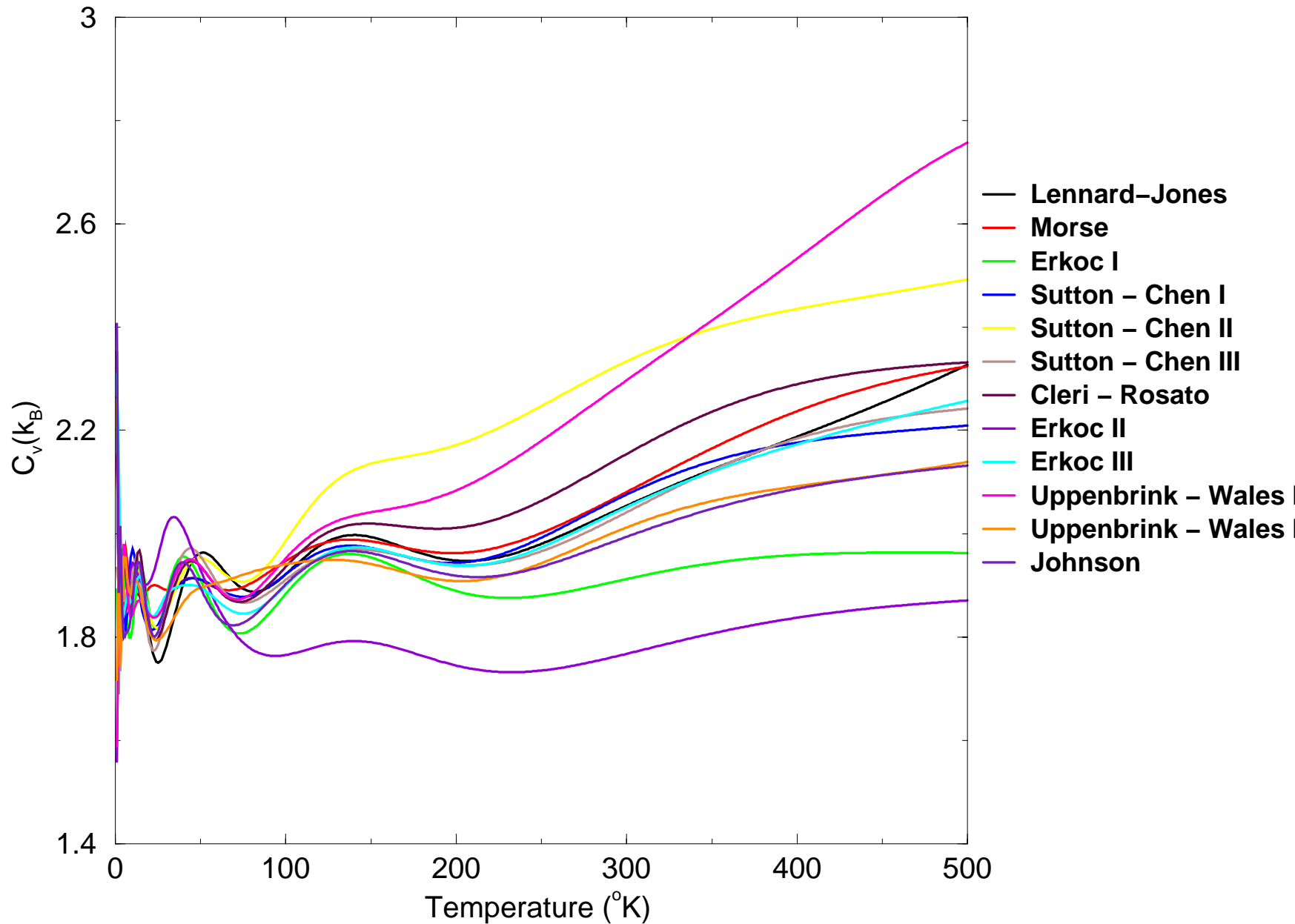
# Energy per atom for the Ni<sub>5</sub> cluster



# $C_v$ per atom for the $Ni_5$ cluster

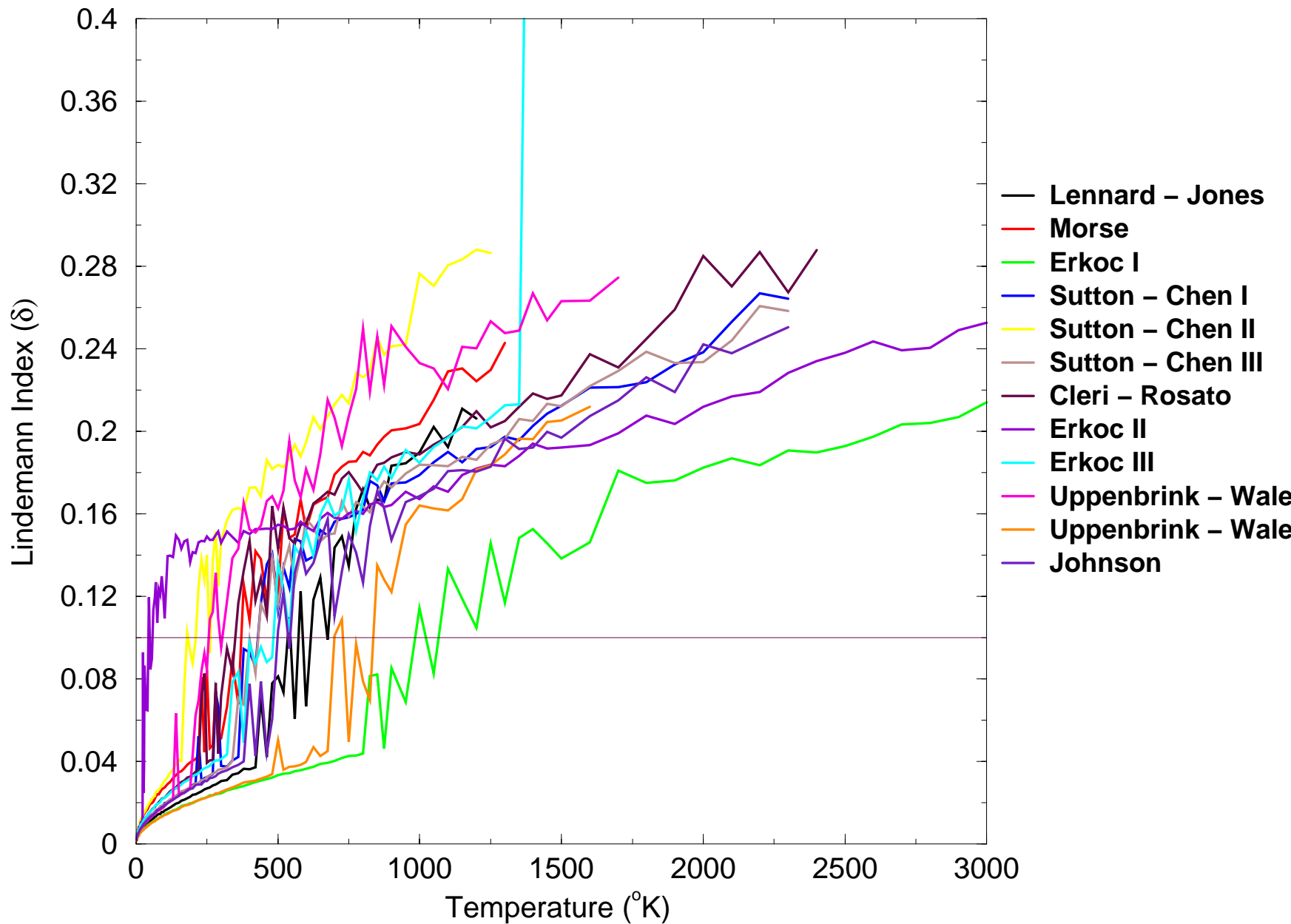


# $C_v$ per atom for the $Ni_5$ cluster

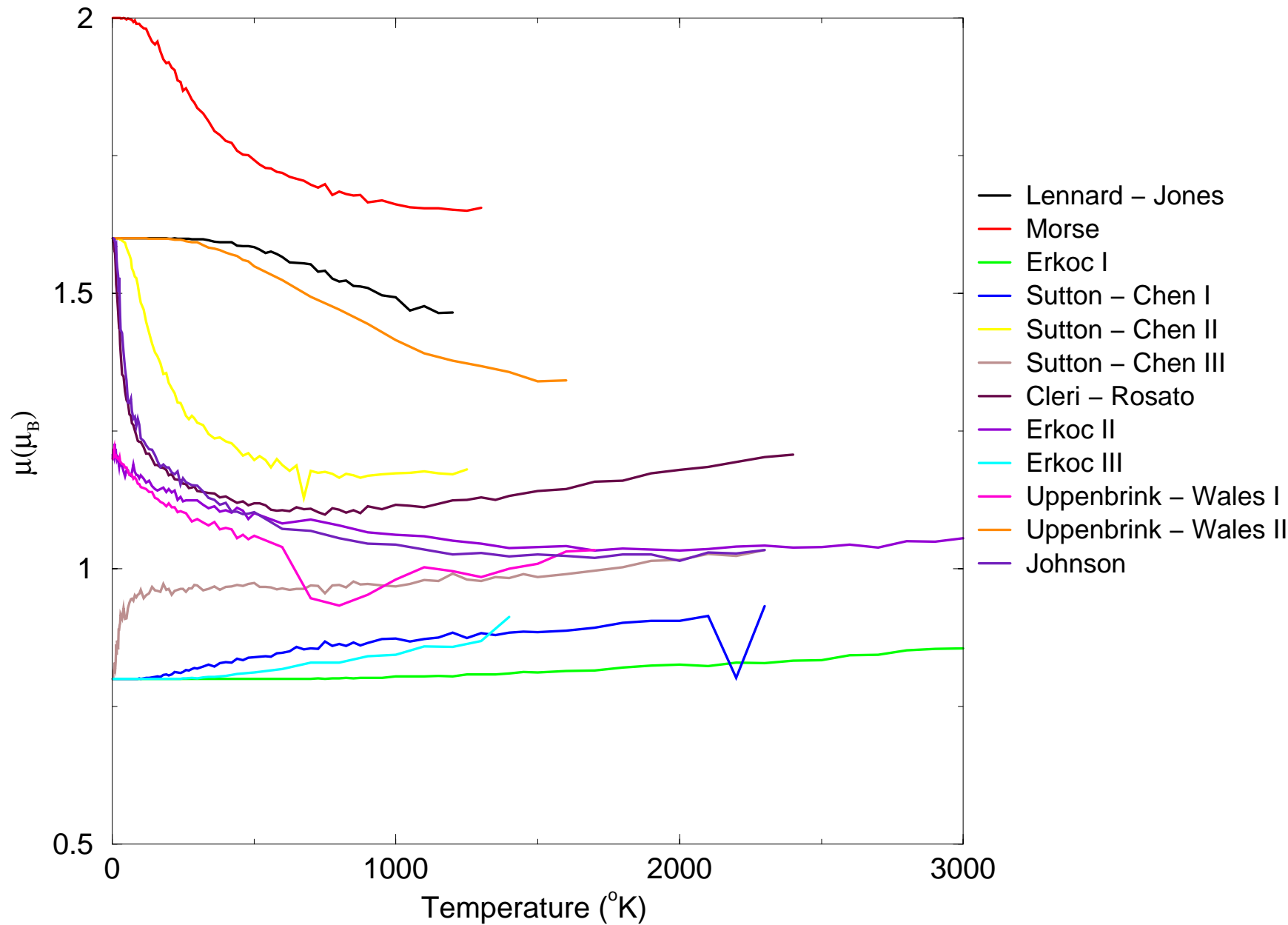




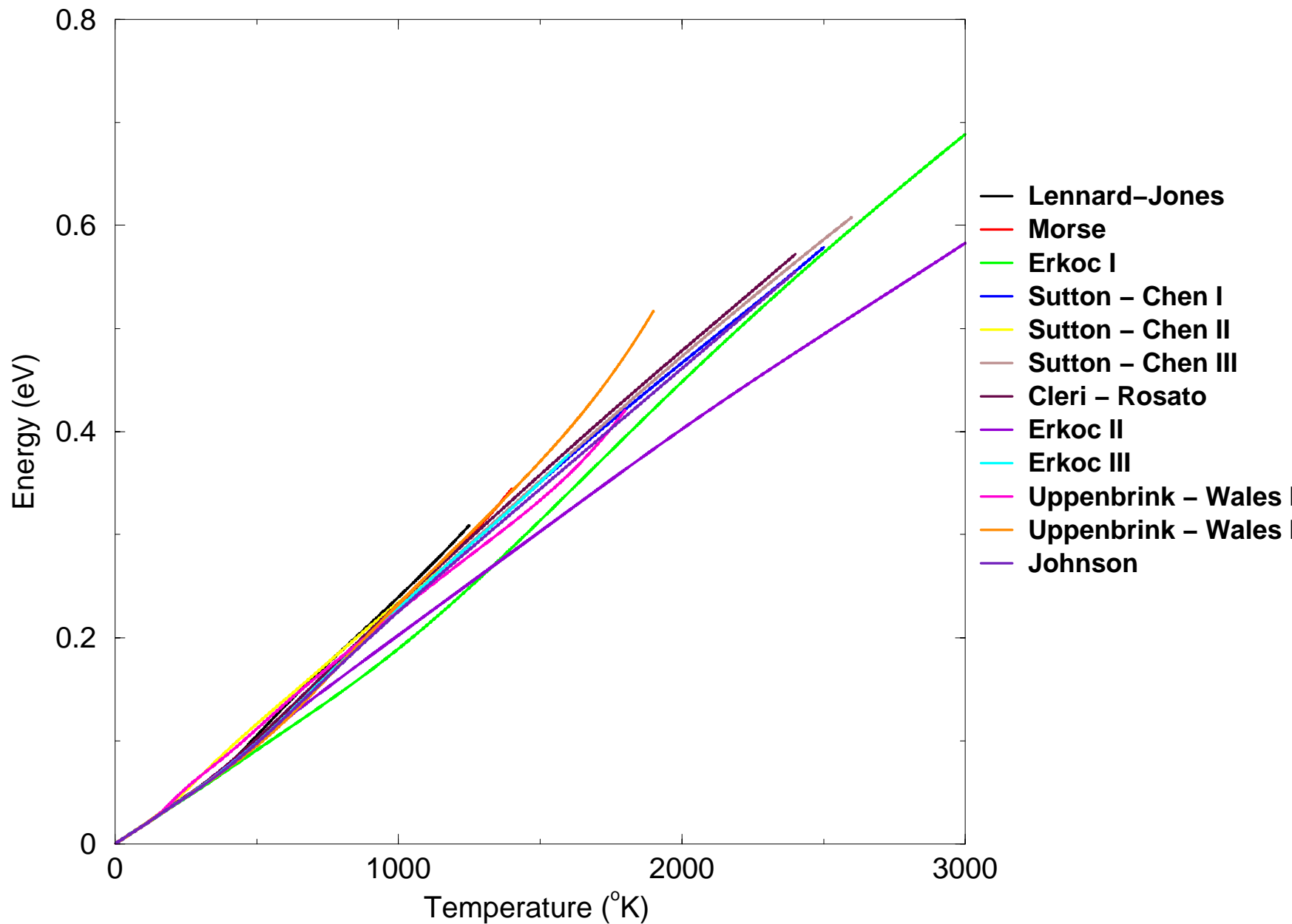
# Lindemann Index for the Ni<sub>5</sub> cluster



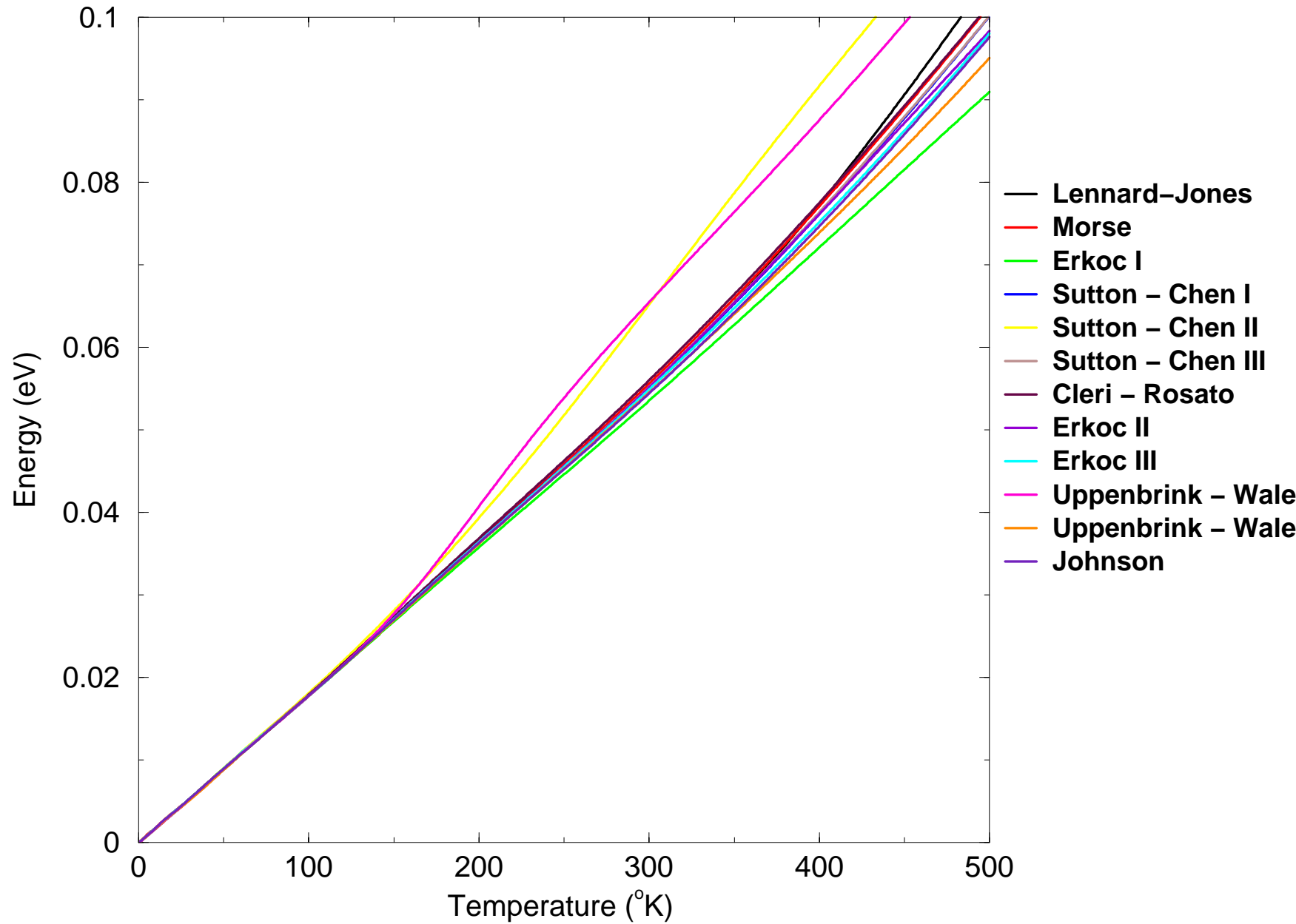
# Magnetic Moment per atom for the Ni<sub>5</sub> cluster



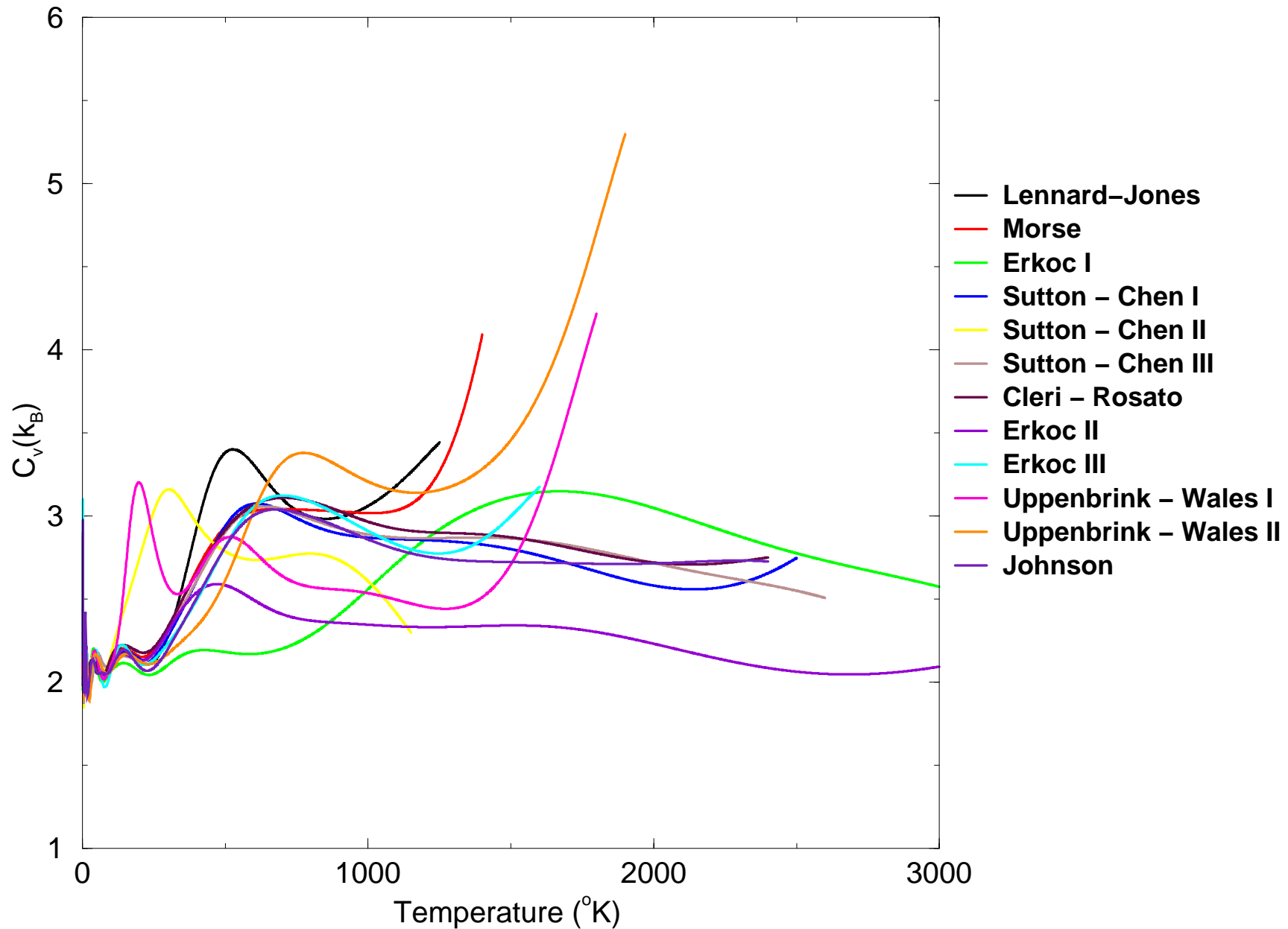
# Energy per atom for the Ni<sub>6</sub> cluster



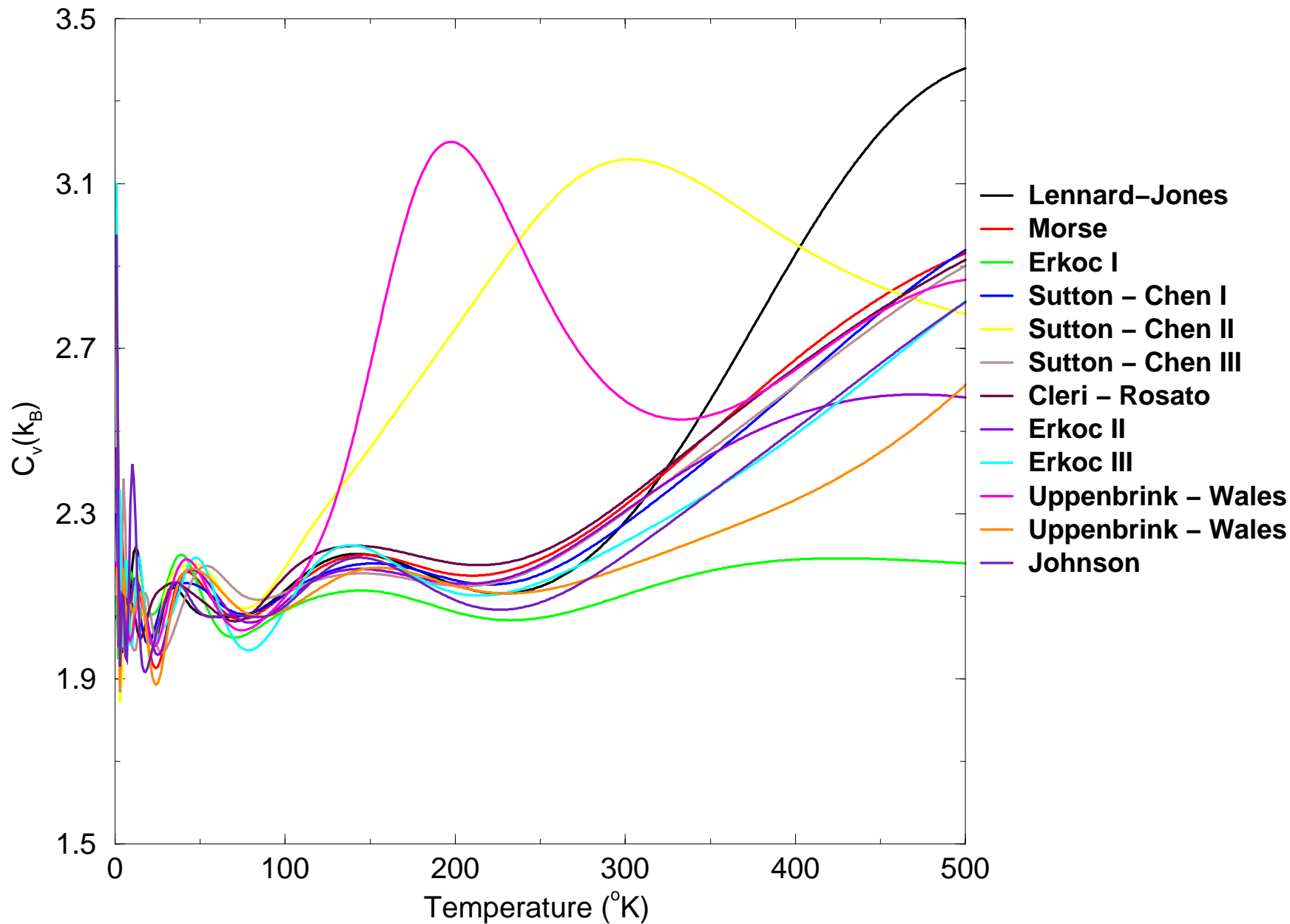
# Energy per atom for the Ni<sub>6</sub> cluster



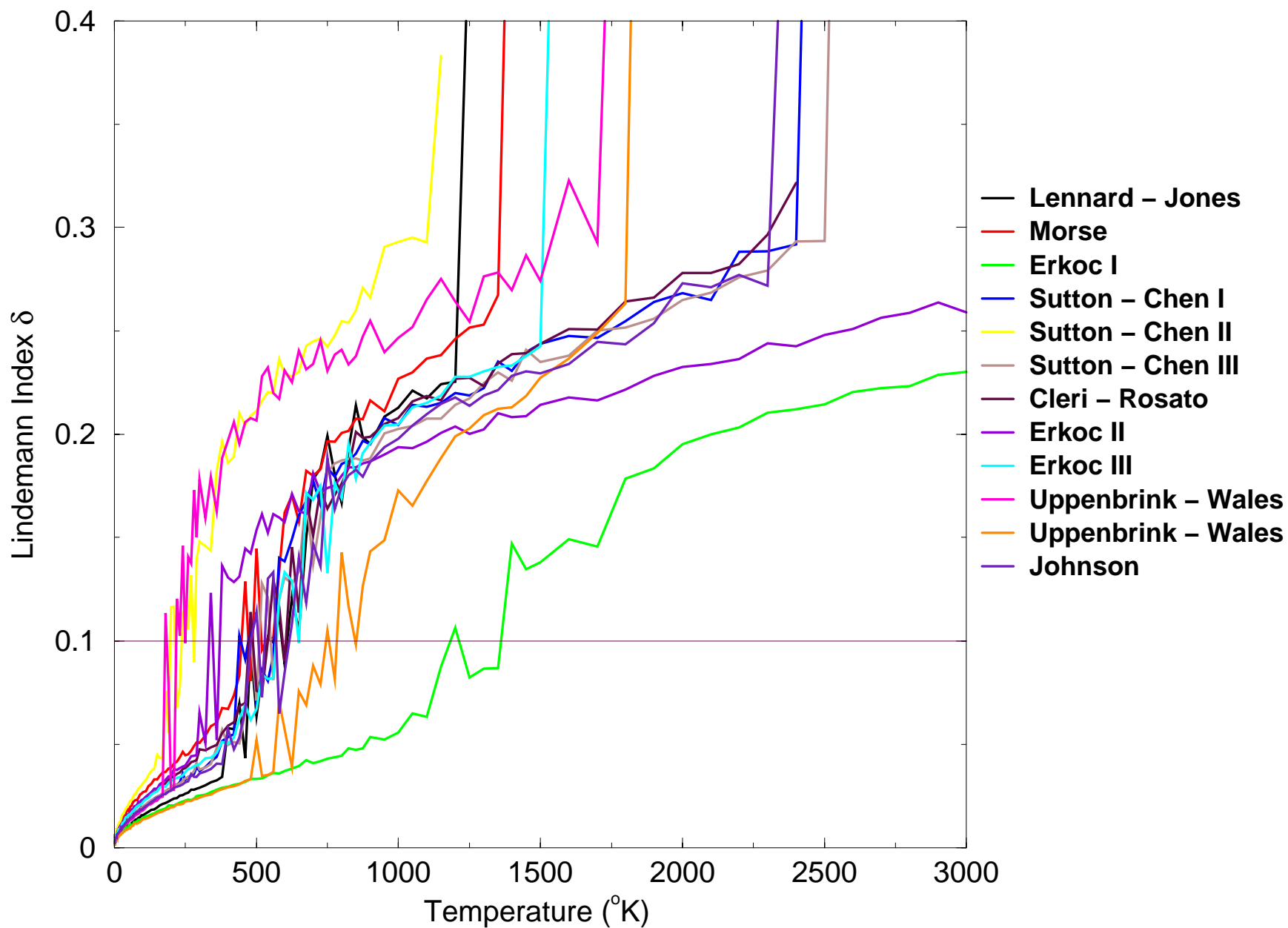
# $C_v$ per atom for the $Ni_6$ cluster



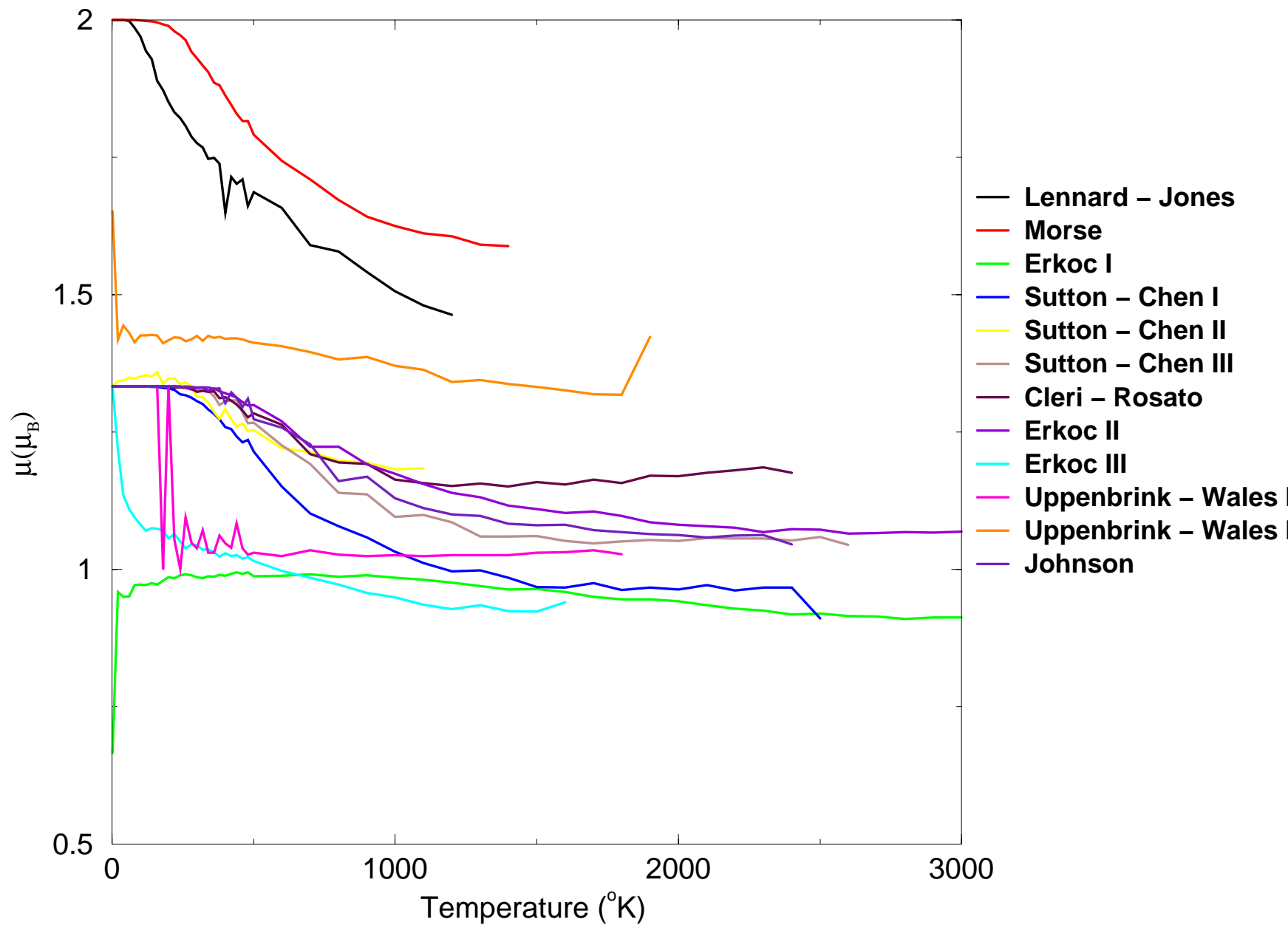
# $C_v$ per atom for the $Ni_6$ cluster



# Lindemann Index for the Ni<sub>6</sub> cluster

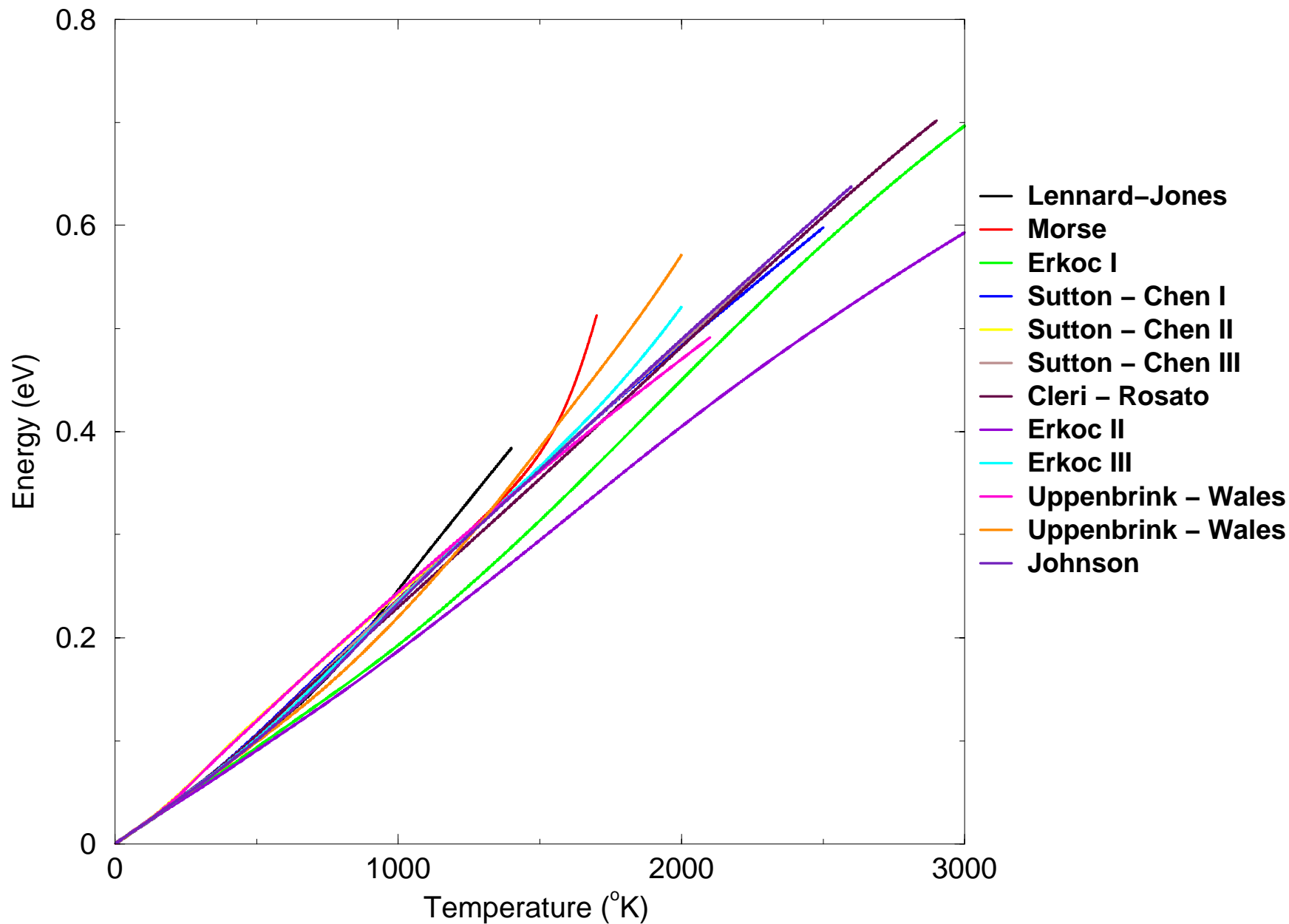


# Magnetic moment per atom for the Ni<sub>6</sub> cluster

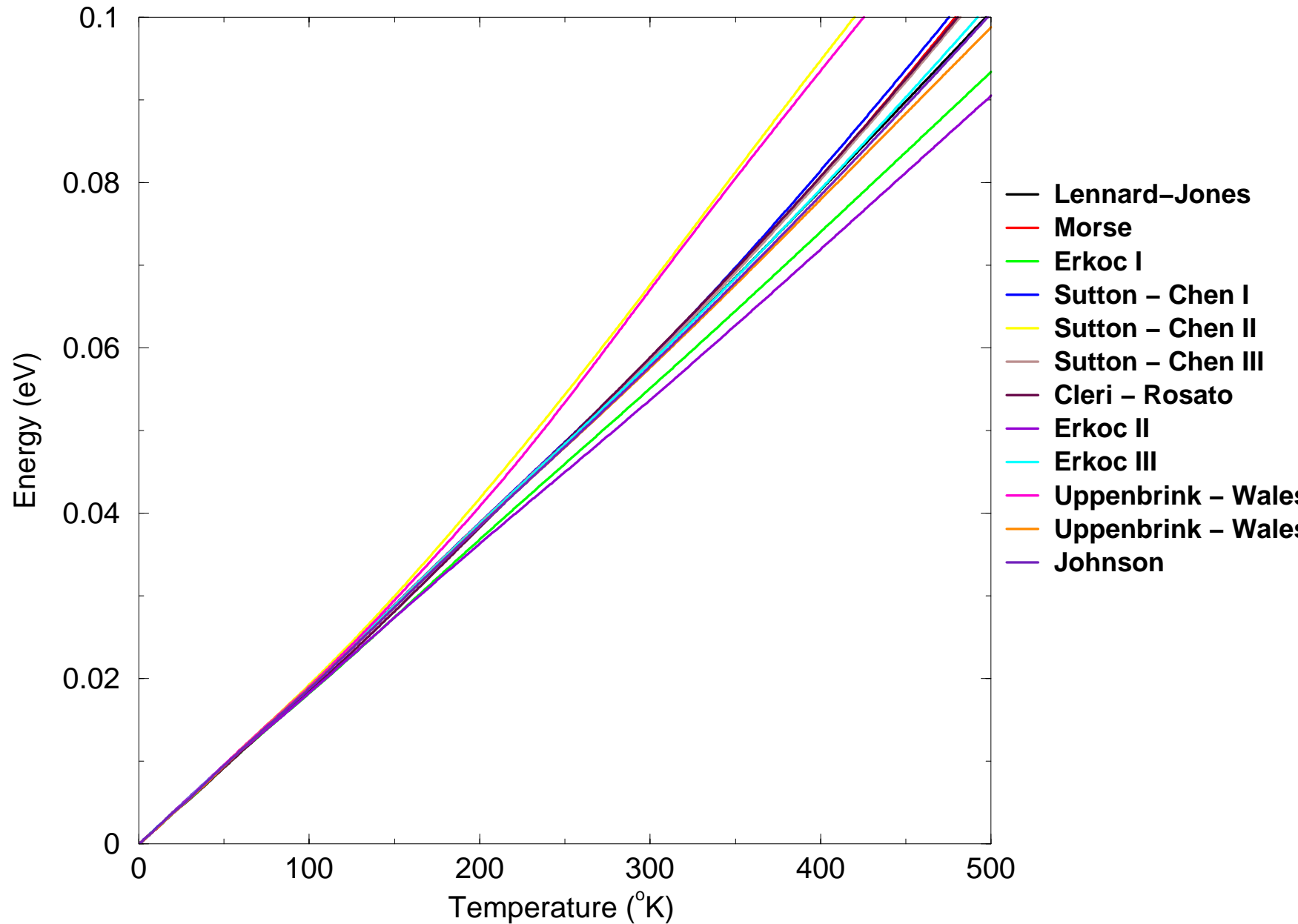




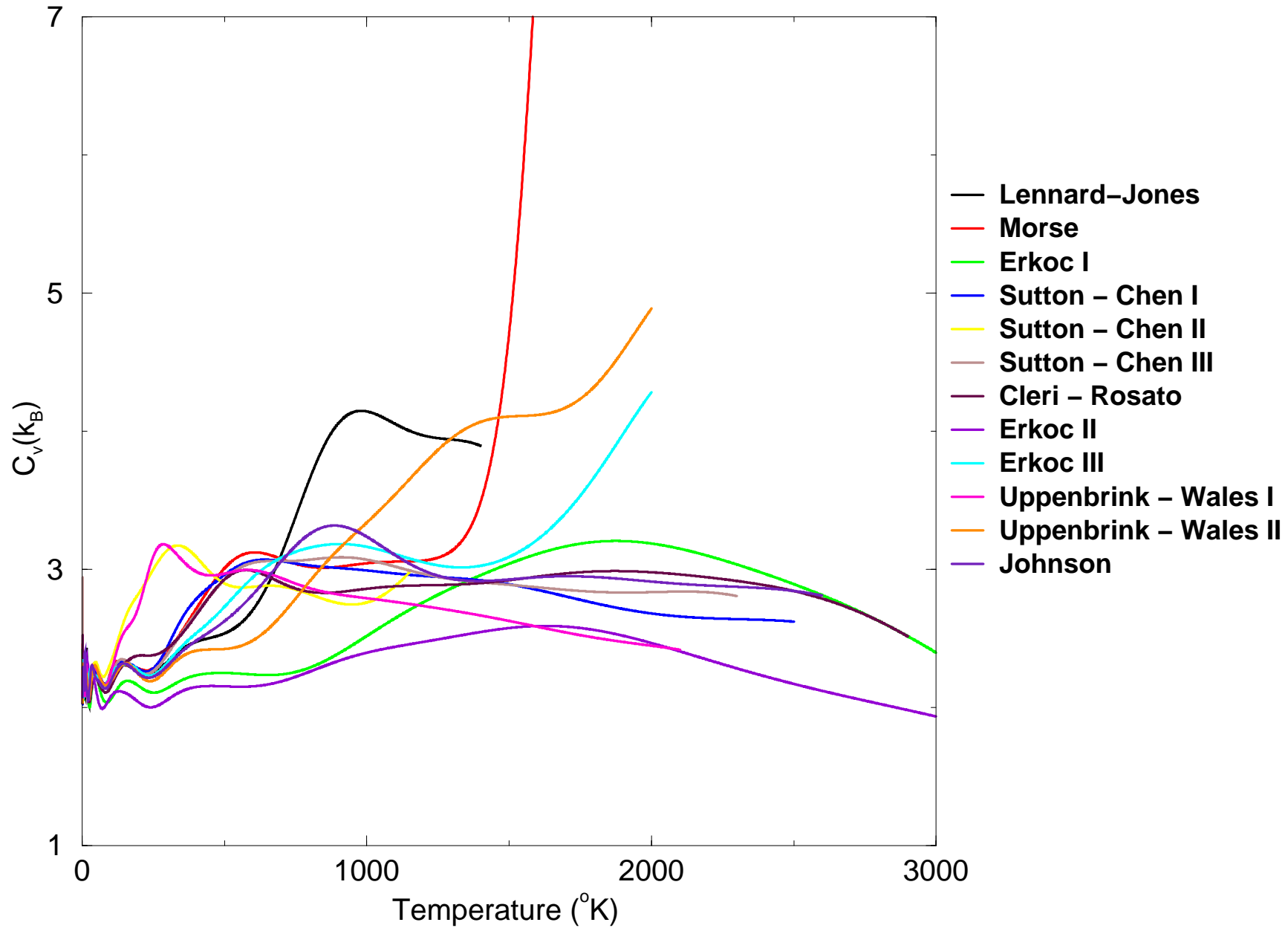
# Energy per atom for the Ni<sub>7</sub> cluster



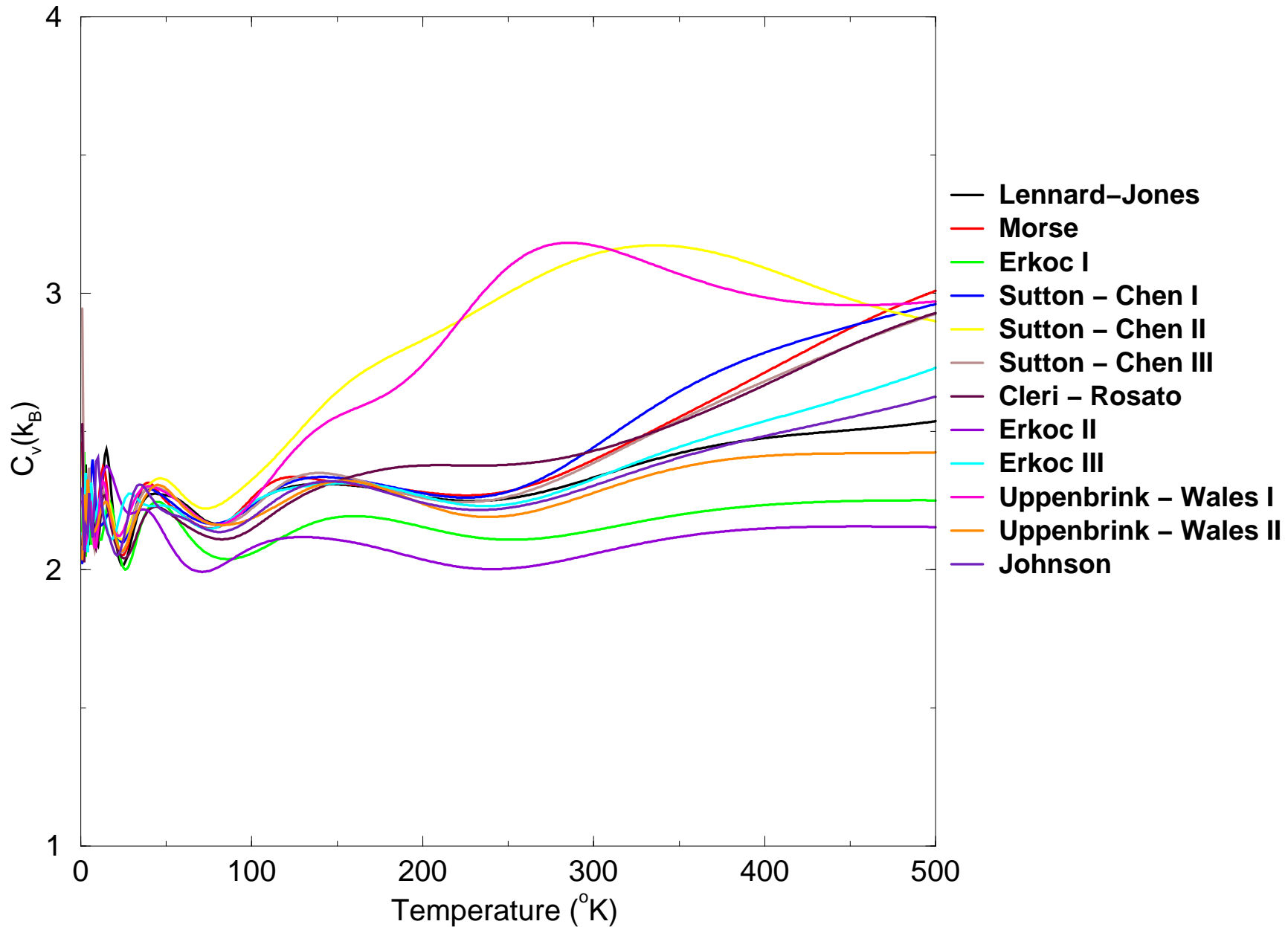
# Energy per atom for the Ni<sub>7</sub> cluster



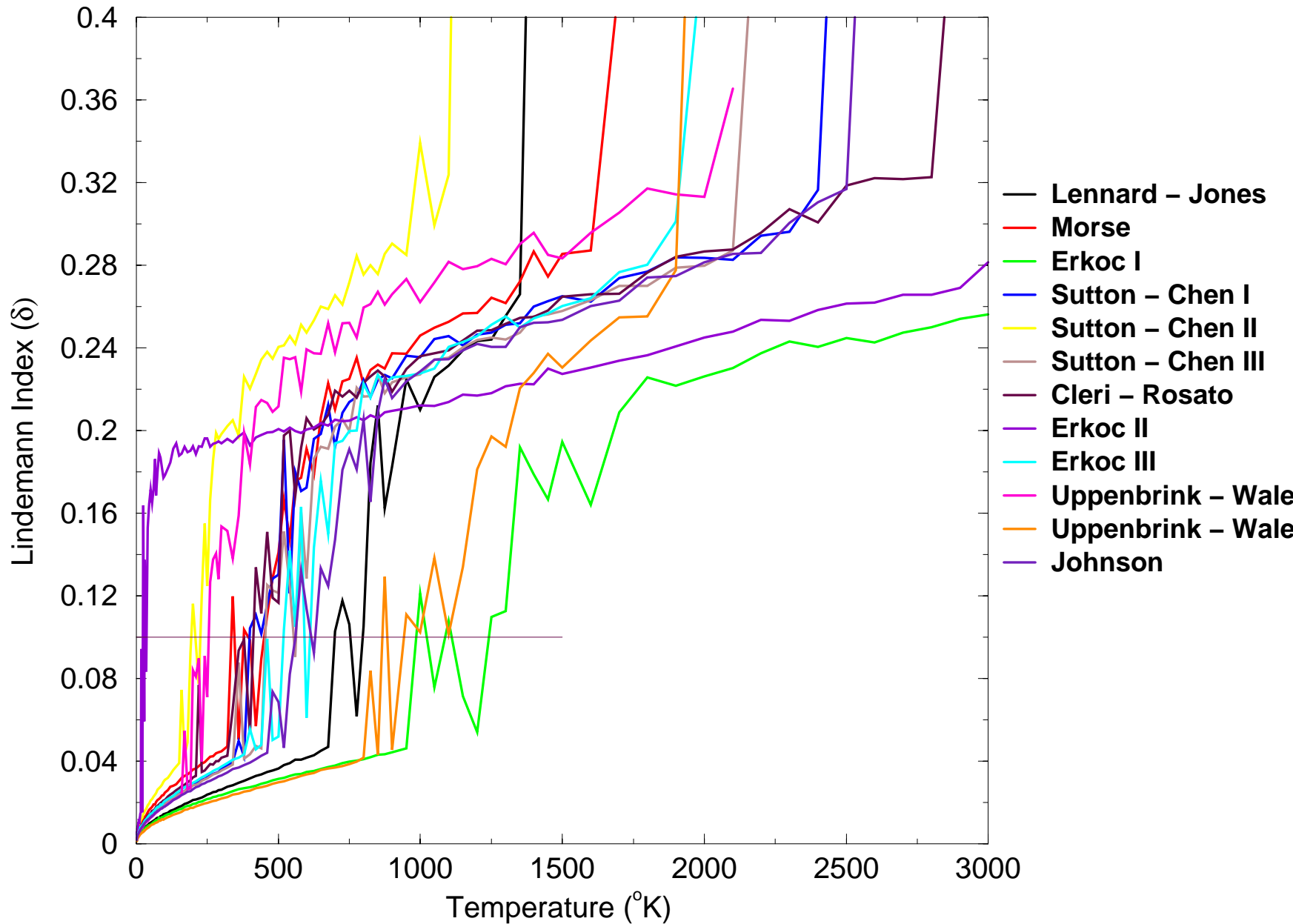
# $C_v$ per atom for the $Ni_7$ cluster



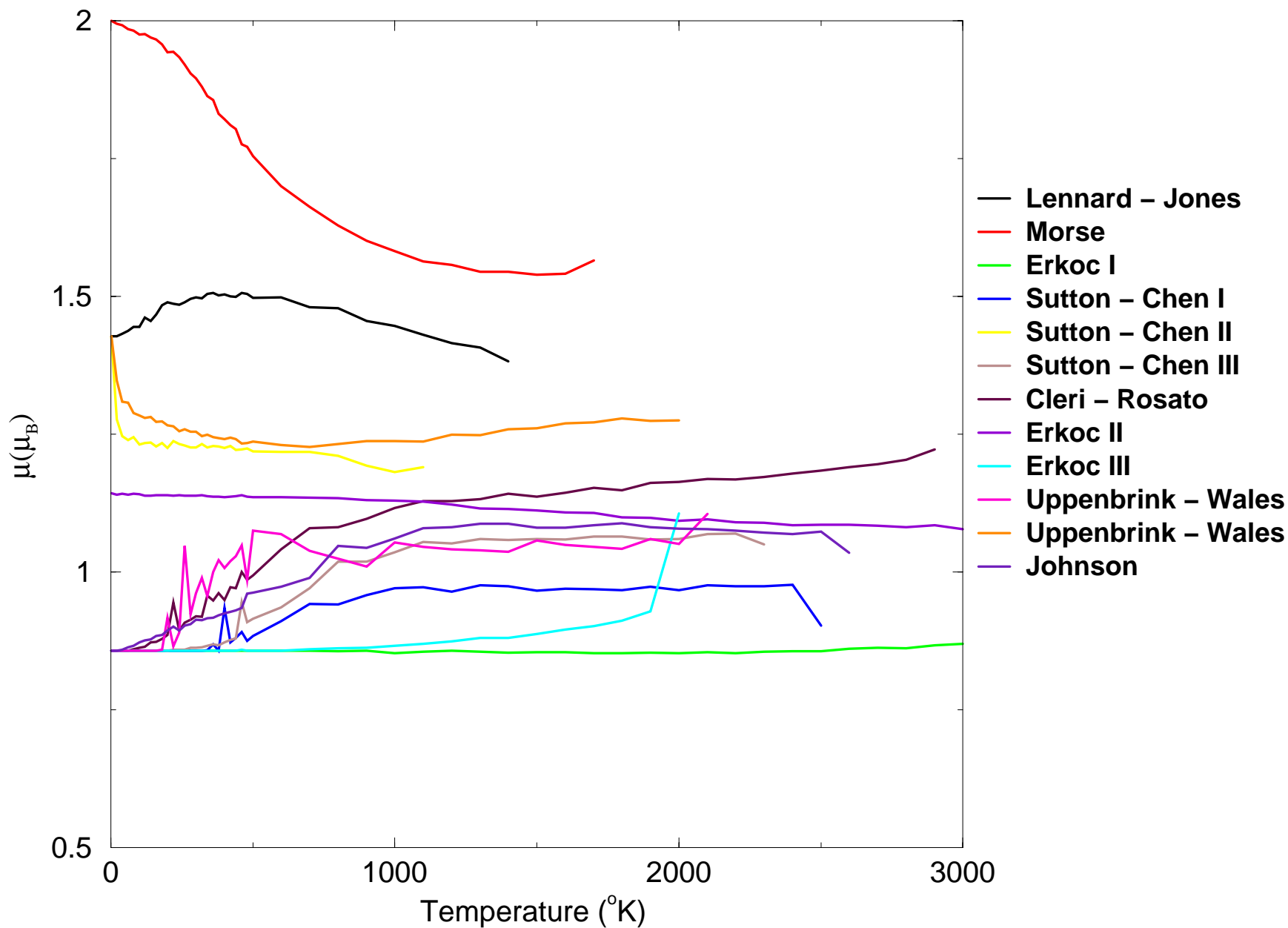
# $C_v$ per atom for the $Ni_7$ cluster



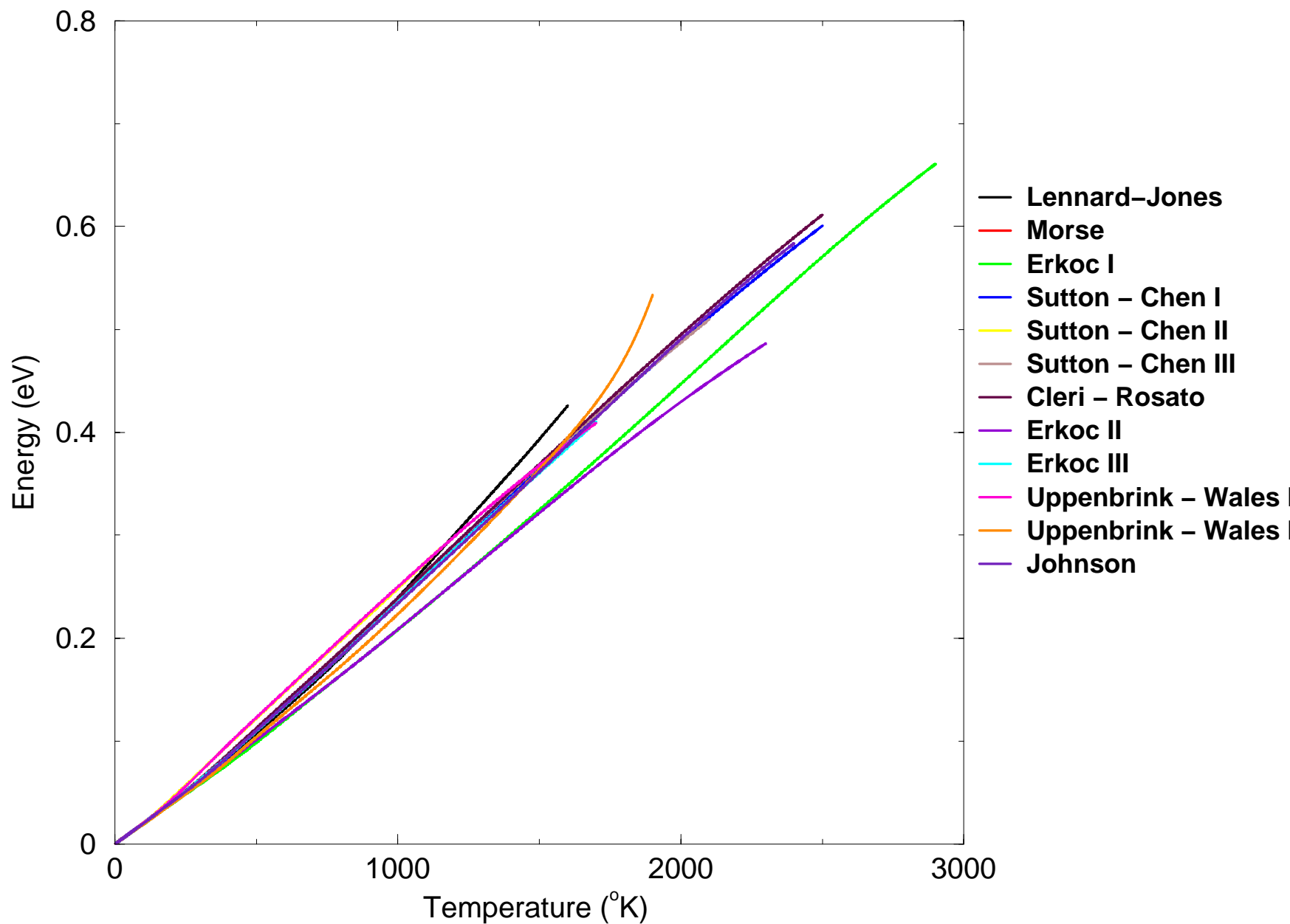
# Lindemann Index for the Ni<sub>7</sub> cluster



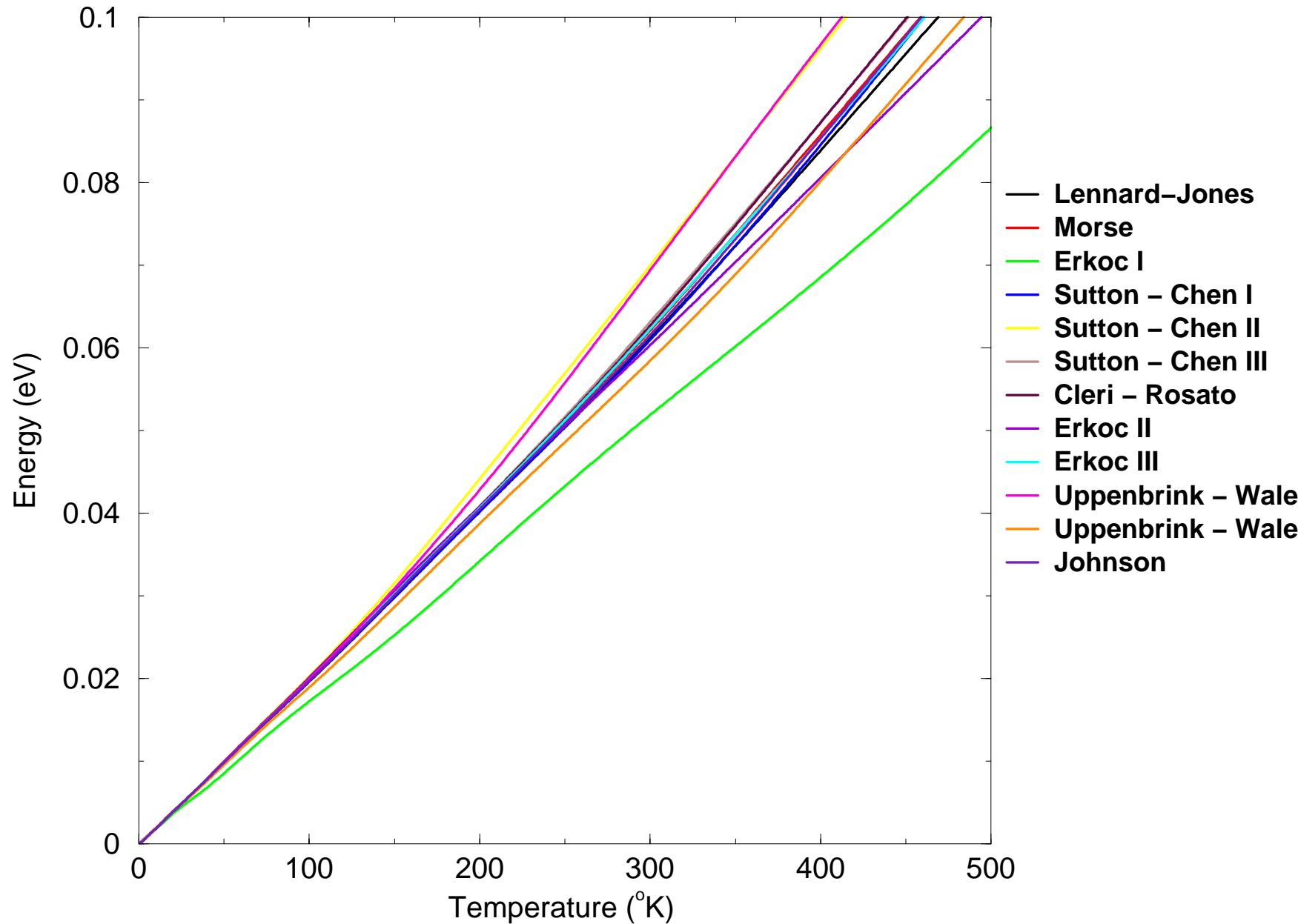
# Magnetic moment per atom for the Ni<sub>7</sub> cluster



# Energy per atom for the Ni<sub>8</sub> cluster

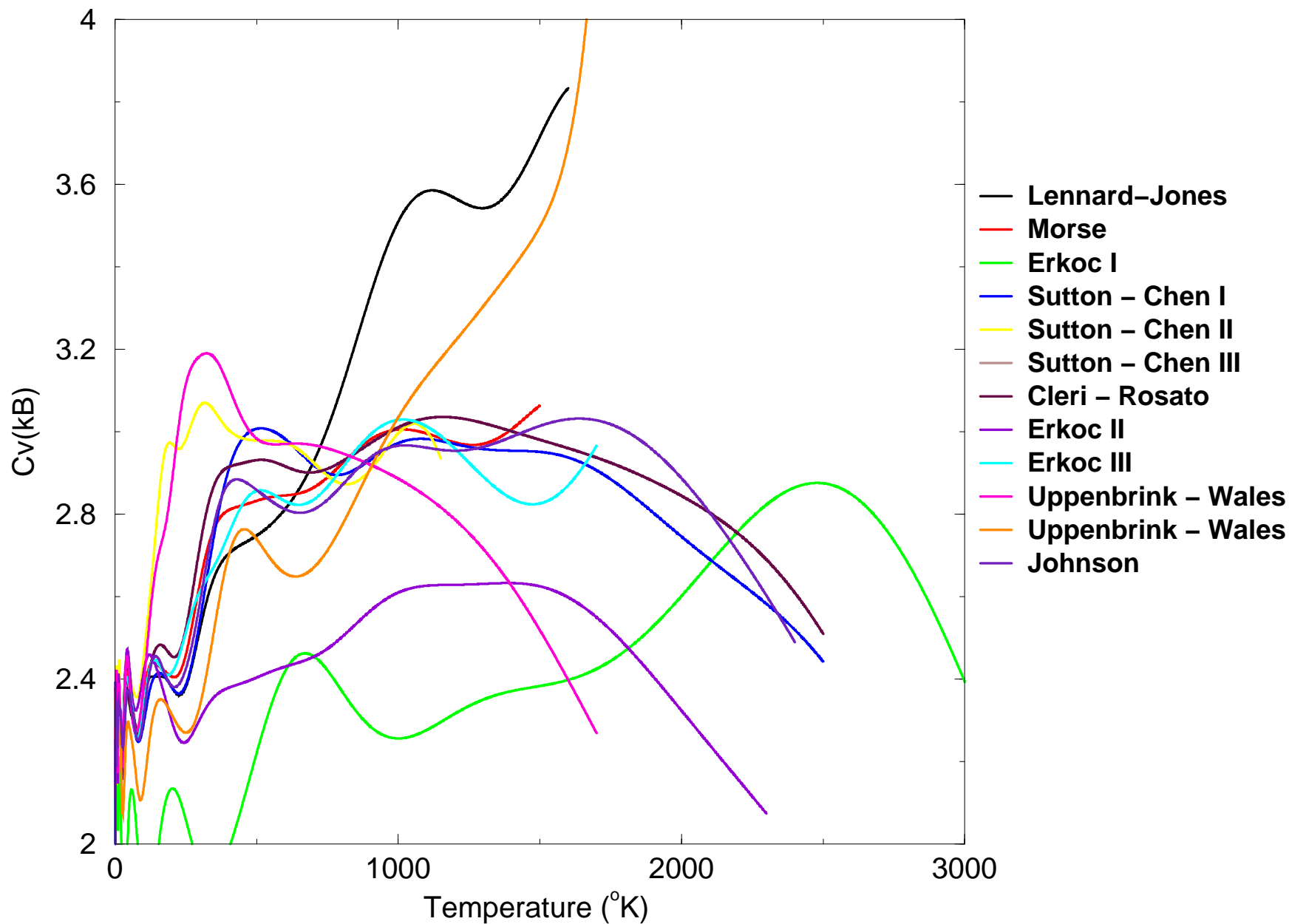


# Energy per atom for the Ni<sub>8</sub> cluster

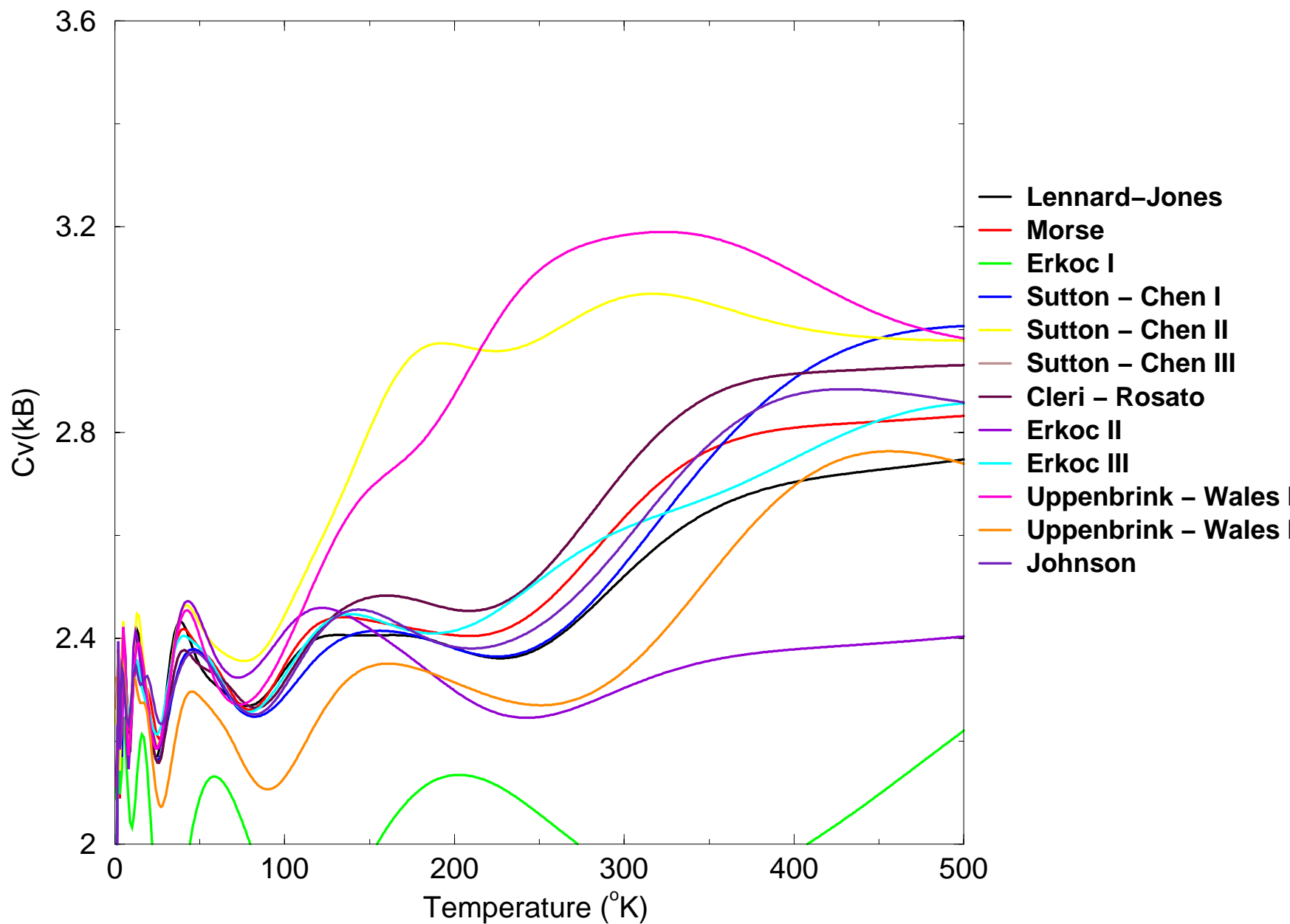




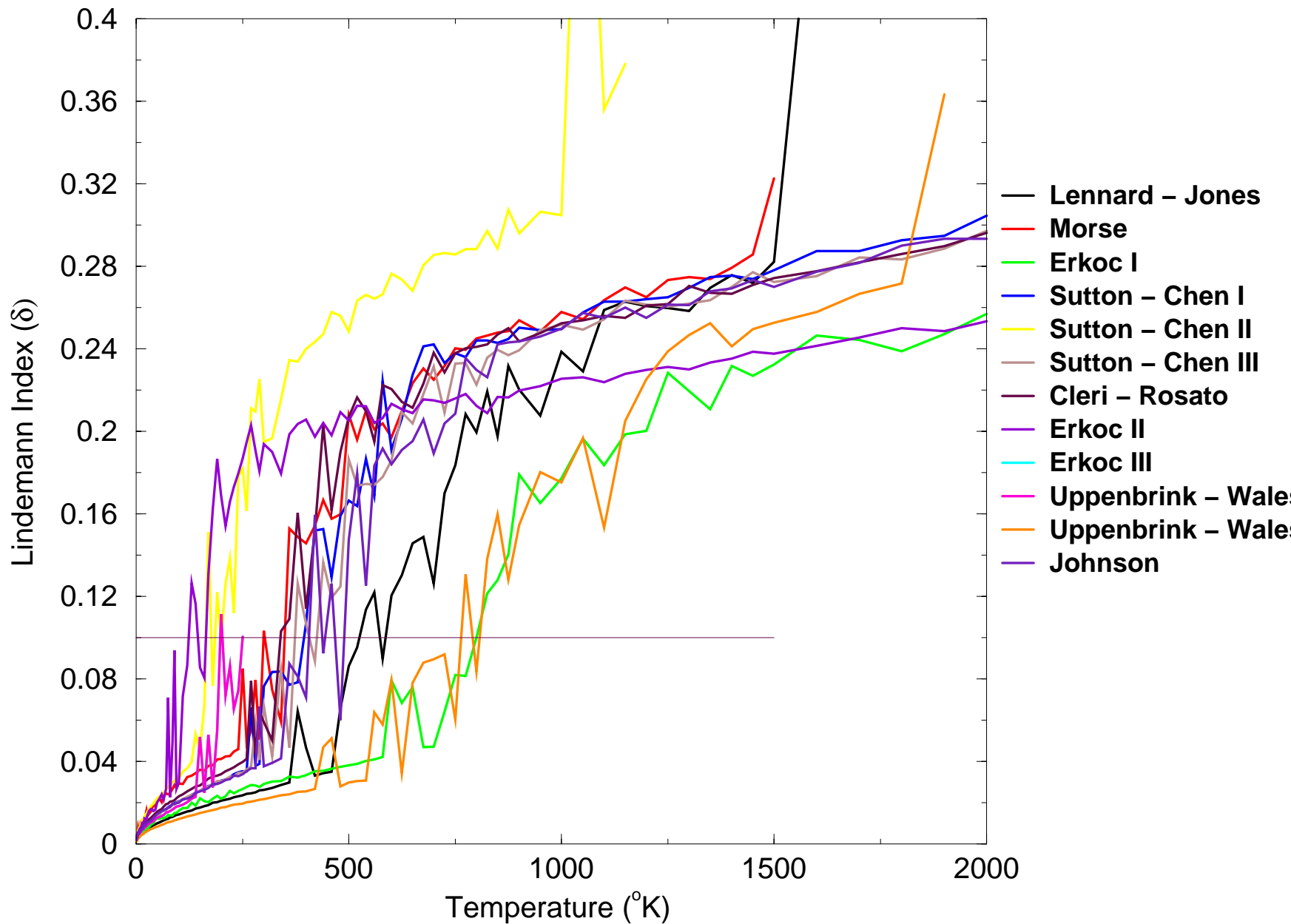
# Cv per atom for the Ni<sub>8</sub> cluster



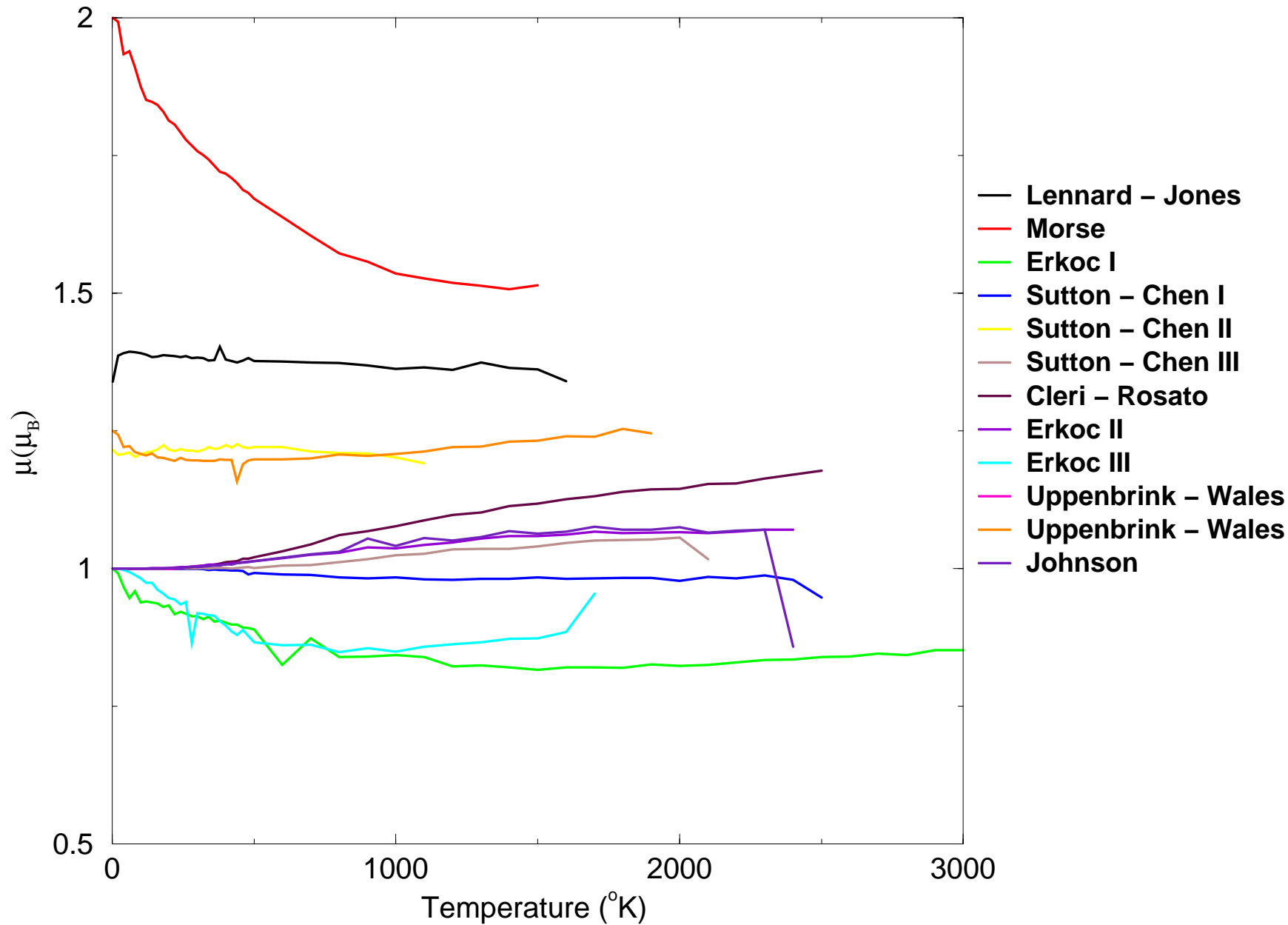
# Cv per atom for the Ni<sub>8</sub> cluster



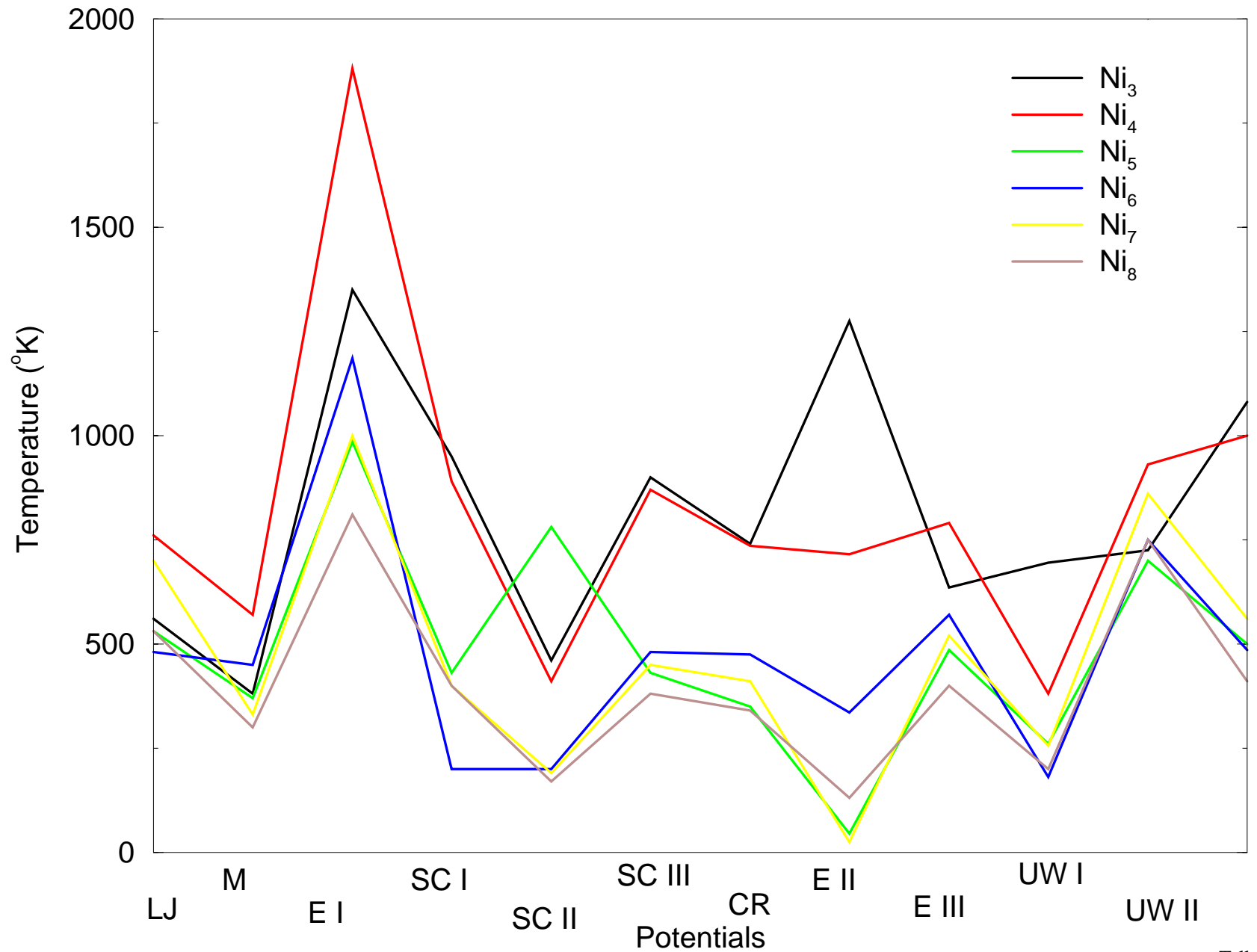
# Lindemann Index for the Ni<sub>8</sub> cluster



# Magnetic moment per atom for the Ni<sub>8</sub> cluster



# Melting Temperature



# Acknowledgments

- Supported through EU-GROWTH research project AMMARE (G5RD-CT-2001-00478)
- Computational Support Dr. S. Stamatiadis

# Δυναμικό **Lennard - Jones**

$$U = \sum_{i>j} 4\epsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^6 \right]$$

Για το  $Ni$

$$\sigma = 2.282 \text{ \AA} \quad \epsilon = 0.51965 eV$$

T.Halicioglu and G.M.Pound, Phys.Stat.Sol.(b), **30**, 619, (1975)

Επιστροφή

# Δυναμικό Morse

$$U = \sum_{i>j} D \left[ e^{-2a(r_{ij}-r_0)} - 2e^{-a(r_{ij}-r_0)} \right]$$

Για το Ni

$$D = 0.4279eV, \quad a = 1.3917 \text{ \AA}^{-1}, \quad r_0 = 2.793\text{\AA}$$

P.G.Flahive and W.R.Graham, Surf.Sci.**91**, 449, (1980)

Επιστροφή



# Δυναμικό Erkoс I

$$U = A \sqrt{\frac{\beta_1 N - \beta_2}{N}} \sum_{i>j} \left[ \left( \frac{r_0}{r_{ij}} \right)^{2n} e^{-2a(r_{ij}/r_0)^2} - \left( \frac{r_0}{r_{ij}} \right)^n e^{-a(r_{ij}/r_0)^2} \right]$$

Για το  $Ni$

$$A = 8.28eV, a = \ln 2, r_0 = 2.20\text{\AA}, n = 2.8947, \\ \beta_1 = 0.081, \beta_2 = 1.523$$

S. Erkoс ...

Επιστροφή

# Δυναμικό Sutton - Chen

$$U = \epsilon \left[ \sum_{i>j} \left( \frac{a}{r_{ij}} \right)^n - c \sum_i \left( \sum_{j \neq i} \left( \frac{a}{r_{ij}} \right)^m \right)^{1/2} \right]$$

Για το  $Ni$

- $\epsilon = 0.015707eV$ ,  $a = 3.52 \text{ \AA}$ ,  $c = 39.432$ ,  $n = 9$ ,  $m = 6$   
A.P.Sutton and J.Chen, Philos. Mag. Lett. **61**, 139, (1990)
- $\epsilon = 1.1340480eV$ ,  $a = 2.15281165\text{\AA}$ ,  $c = 1.317017$ ,  $n = 9$ ,  
 $m = 6$   
Fitted to Dimer
- $\epsilon = 0.0073767eV$ ,  $a = 3.5157\text{\AA}$ ,  $c = 84.745$ ,  $n = 10$ ,  $m = 5$   
Y.Kimura et al, Phys.Rev. B, **59**, 3527, (1999)

# Δυναμικό Cleri - Rosato

$$U = \sum_{i>j} A e^{-p(r_{ij}/r_0-1)} - \sum_i \left( \sum_{j \neq i} \xi^2 e^{-2q(r_{ij}/r_0-1)} \right)^{1/2}$$

Για το  $Ni$

$$A = 0.0376 eV, \xi = 1.070 eV, p = 16.999, q = 1.189, \\ a_0 = 3.523 \text{Å}, r_0 = a_0 / \sqrt{2} = 2.491 \text{Å}$$

F.Cleri and V.Rosato, Phys.Rev.B, **48**, 22, (1993)

Επιστροφή

# Δυναμικό Erkoç II

$$U = \sum_{i>j} U_{ij} + \sum_{i>j>k} W_{ijk}$$

$$U_{ij} = A \left[ \left( \frac{r_0}{r_{ij}} \right)^{2n} e^{-2a(r_{ij}/r_0)^2} - \left( \frac{r_0}{r_{ij}} \right)^n e^{-a(r_{ij}-r_0)^2} \right]$$

$$W_{ijk} = B(U_{ij}f_{ijk} + U_{jk}f_{jki} + U_{ki}f_{kij})$$

$$f_{ijk} = e^{-(r_{ik}^2 + r_{jk}^2)/r_0^2}$$

Για το  $Ni$

$$A = 8.28eV, a = \ln 2, r_0 = 2.20\text{\AA}, n = 2.892470,$$

$$\beta = -1.290433$$

S.Erkoç, Phys.Stat.Sol.(b), **152**, 447, (1989); *ibid* **155**, 461, (1989)

# Δυναμικό Erkos III

$$U = \sum_{i>j} U_{ij} + \sum_{i>j>k} W_{ijk}$$

$$U_{ij} = C_2 A \left[ \left( \frac{r_0}{r_{ij}} \right)^{2n} e^{-2a(r_{ij}/r_0)^2} - \left( \frac{r_0}{r_{ij}} \right)^n e^{-a(r_{ij}-r_0)^2} \right]$$

$$W_{ijk} = C_3 (U_{ij} f_{ijk} + U_{jk} f_{jki} + U_{ki} f_{kij})$$

$$f_{ijk} = e^{-(r_{ik}^2 + r_{jk}^2)/r_0^2}$$

Για το  $Ni$

Ίδιες παράμετροι με Erkos II

$$C_2 = 0.2860750 \quad C_3 = -0.1688664$$

S.Erkoc, Phys.Stat.Sol.(b), **161**, 211, (1990)

# Δυναμικό Uppenbrink - Wales

$$U = \sum_{i>j} 4\epsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - 2 \left( \frac{\sigma}{r_{ij}} \right)^6 \right] + \sum_{i>j>k} Z \frac{1 + 3 \cos \theta_i \cos \theta_j \cos \theta_k}{(r_{ij} r_{jk} r_{ki})^3}$$

Για το  $Ni$

- $\epsilon = 1.136 eV$ ,  $\sigma = 2.225 \text{\AA}$ ,  $Z = Z^* \epsilon \sigma^9$ ,  $Z^* = 0.393$
- $\epsilon = 0.613 eV$ ,  $\sigma = 2.508 \text{\AA}$ ,  $Z = Z^* \epsilon \sigma^9$ ,  $Z^* = -0.059$

J.Uppenbrink and D.J.Wales, J.Chem.Phys., **96**,8520, (1992)

Επιστροφή

# Δυναμικό Johnson (EAM)

$$U = \sum_i F(\rho_i) + \sum_{i>j} \phi_e e^{-\gamma(r/r_e-1)}$$

$$F(\rho) = -E_c \left( 1 - \ln \left( \frac{\rho}{\rho_e} \right)^{\alpha/\beta} \right) \left( \frac{\rho}{\rho_e} \right)^{\alpha/\beta} - 6\phi_e \left( \frac{\rho}{\rho_e} \right)^{\gamma/\beta}$$

$$\rho_i = \sum_j f_e e^{-\beta(r/r_e-1)}$$

Για το Ni

$$f_e = 0.41, \phi_e = 0.74eV, \alpha = 4.98, \beta = 6.41, \gamma = 8.86, \\ E_c = 4.45eV$$

R.A.Johnson, Phys.Rev. B, **39**, 12554, (1989)

Επιστροφή

# Επίλυση Εξισώσεων

## Gear corrector - predictor algorithm

- 5ης τάξης για την 1
- 4ης τάξης για τη 2
- Χρονικό βήμα  $\delta t = 1 fsec$
- Αριθμός βημάτων =  $10^7$

$$\Rightarrow \mathbf{r}_i(\mathbf{t}), \mathbf{v}_i(\mathbf{t}), i = 1, 2, \dots, N \Rightarrow E(t) = V(\{\mathbf{r}_i(t)\}) + \sum_i \frac{1}{2} m \mathbf{v}_i^2$$

Αρχικές συνθήκες

$$(1) \mathbf{v}_i = \sqrt{\frac{N-2}{N} \frac{k_B T}{m}} \mathbf{x}(\text{Gauss rnd.}) \quad \mathbf{r}_i = \mathbf{r}_0 + \frac{\hbar}{k_B \Theta_D} \mathbf{v}_i$$

$$(2) \quad \mathbf{v}_i^{new} = \mathbf{v}_i - \mathbf{v}_{cm} - \omega \mathbf{X}(\mathbf{r}_i - \mathbf{r}_{cm})$$



# Στατιστική Φυσική

Πιθανότητα να βρεθεί το cluster με ενέργεια  $E_i$  όταν η θερμοκρασία είναι  $T_j$

$$p_{ij} = \frac{n_{ij}}{N_j} = \frac{\Delta\Gamma_i e^{-\beta_j E_i}}{\sum_{E_i} \Delta\Gamma_i e^{-\beta_j E_i}}$$

$\Delta\Gamma_i$  = Αριθμός καταστάσεων του cluster με ενέργεια  $E_i$ ,  
 $E_n = E_0 + n\delta E$

$$\ln \frac{n_{ij}}{N_j} = \ln \Delta\Gamma_i - \beta_j E_i + \ln Z_j$$

$i = 1, 2, \dots, N$ , (ενέργειες)       $j = 1, 2, \dots, M$  (θερμοκρασίες)

Σύστημα  $N \times M$  εξισώσεων με  $N+M$  αγνώστους

# Multiple Histogram Method

$$R_{ij} = \ln \frac{n_{ij}}{N_j} - \ln \Delta\Gamma_i + \beta_j E_i - \ln Z_j$$

Αν δεν υπήρχαν σφάλματα  $R_{ij} = 0$

↓

Ελαχιστοποίηση σφαλμάτων

$$\chi^2 = \sum_{i=1}^N \sum_{j=1}^M n_{ij} R_{ij}^2 = \min$$

$$\frac{\partial \chi^2}{\partial \ln \Delta\Gamma_i} = 0, \quad \frac{\partial \chi^2}{\partial \ln Z_j} = 0$$

Γραμμικό σύστημα (N+M) εξισώσεων με (N+M) αγνώστους  
⇒  $\Delta\Gamma_i$  Επιστροφή

# Tight Binding Hamiltonian

$$\mathcal{H} = \begin{pmatrix} \mathcal{H}_{\uparrow\uparrow} & \mathcal{H}_{\uparrow\downarrow} \\ \mathcal{H}_{\downarrow\uparrow} & \mathcal{H}_{\downarrow\downarrow} \end{pmatrix}$$

$$\mathcal{H}_{\uparrow\uparrow} = H + uI, \quad \mathcal{H}_{\downarrow\downarrow} = H - uI, \quad \mathcal{H}_{\uparrow\downarrow} = \mathcal{H}_{\downarrow\uparrow} = 0$$

$$H = \begin{pmatrix} H_{11} & H_{12} & \dots & H_{1N} \\ H_{21} & H_{22} & \dots & H_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ H_{N1} & H_{N2} & \dots & H_{NN} \end{pmatrix}$$

Επιστροφή